

## Density functional theory study of vibrational spectra, and assignment of fundamental modes of dacarbazine

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**Abstract.** The FTIR and FT Raman spectra of dacarbazine were recorded in the regions 4000–400 and 3500–100 cm<sup>-1</sup>, respectively. The optimized geometry, wavenumber, polarizability and several thermodynamic properties of dacarbazine were studied using *ab initio* Hartree–Fock, MP2 and DFT methods. A complete vibrational assignment aided by the theoretical harmonic wavenumber analysis was proposed. The calculated harmonic vibrational frequencies were compared with experimental FTIR and FT Raman spectra. Based on the comparison between calculated and experimental results and the comparison with related molecules, assignments of fundamental vibrational modes were made. The X-ray geometry and experimental frequencies were compared with the results of theoretical calculations.

**Keywords.** FTIR; FT-Raman; density functional theory; dacarbazine.

### 1. Introduction

Dacarbazine, used as antineoplastic in the treatment of tumors. It belongs to the group of medicines called alkylating agents. It is used in the treatment of cancer of the lymph system and malignant melanoma a type of skin cancer. Dacarbazine, (DTIC-NSC-45388) is the single most active agent for the treatment of malignant melanoma. In addition to dacarbazine, other dimethyltriazenes have shown to demonstrate anti-tumor properties.<sup>1–5</sup> Literature survey reveals that to the best of our knowledge, no *ab initio* HF/MP2/DFT frequency calculations of dacarbazine have been reported so far.

It is difficult to interpret the spectra of this molecule because of their complexity and low symmetry. In the interest of these physiological applications and the consequent in their qualitative and quantitative characterization in aqueous solution, the quantum mechanical calculations of this compound were thoroughly investigated. In this study, density functional theory (DFT) by using B3LYP hybrid functional, Moller–Plesset (MP2) and *ab initio* Hartree–Fock (HF) computations of the vibrational spectrum, the molecular geometry, the atomic charges and mole-

cular polarizability calculations were carried out for dacarbazine molecule. The experimental geometric data of the molecule were taken from the Cambridge crystallographic database.<sup>6</sup> *Ab initio* HF and density functional theory (DFT) calculations were performed to support our wavenumber assignment. Density functional calculations are reported to provide excellent vibrational wavenumber of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity.<sup>7–10</sup>

### 2. Experimental

The compound dacarbazine was purchased from Messrs Sigma–Aldrich Chemical Company, USA with more than 98% purity and was used as such without further purification to record FTIR and FT Raman spectra. The FTIR spectrum of the compound was recorded in the region 4000–400 cm<sup>-1</sup> in evacuation mode on Bruker IFS 66V spectrophotometer using KBr pellet technique (solid phase) with 4.0 cm<sup>-1</sup> resolution. The FT Raman spectrum was recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the region 3500–100 cm<sup>-1</sup> on Bruker IFS 66V spectrometer equipped with FRA

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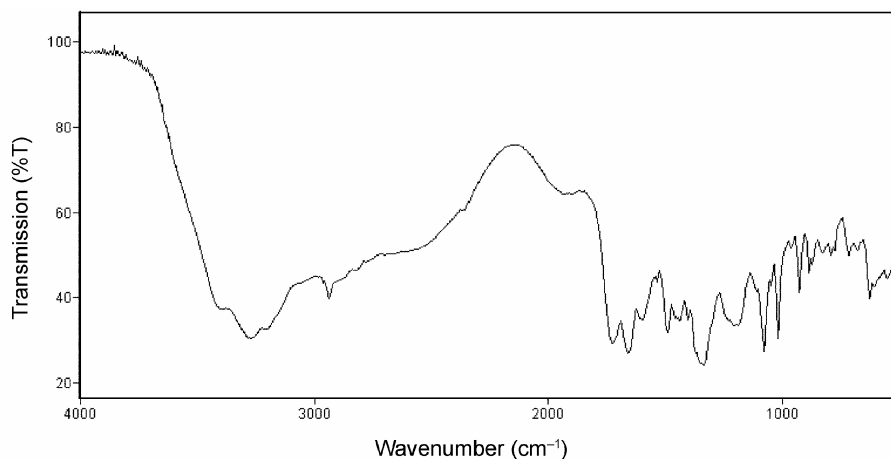


Figure 1. FTIR spectrum of dacarbazine.

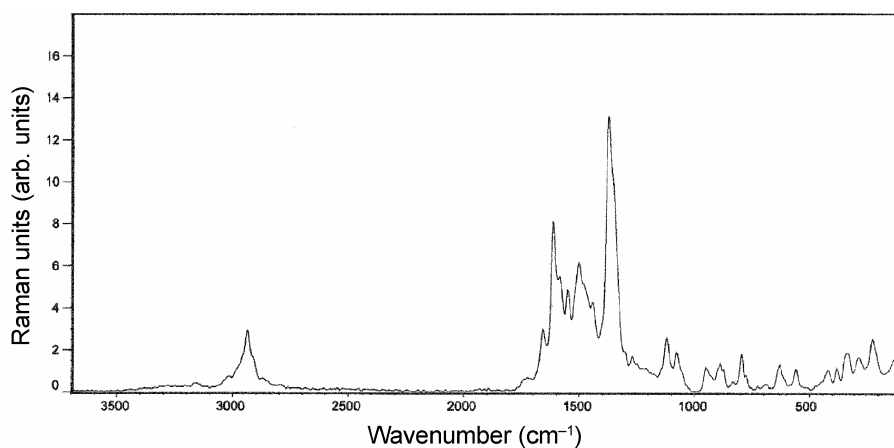


Figure 2. FT-Raman spectrum of dacarbazine.

106 FT Raman module accessory. The experimental FTIR and FT Raman spectra of dacarbazine are presented in figures 1 and 2.

### 3. Computational methods

The entire calculations performed at HF, MP2 and B3LYP levels on an AMD 4000+/3.2 GHz personal computer using Gaussian 03 W program package.<sup>11</sup> Initial geometry generated from standard geometrical parameters minimized without any constraint in the potential energy surface at HF level, adopting the standard 6-31G basis set. The optimized structural parameters used in the vibrational wavenumber calculations at the HF and DFT levels to characterize all stationary points as minima. Then, vibrationally averaged nuclear positions of dacarbazine used for harmonic vibrational wavenumber calculations resulting in IR and Raman wavenumbers together with in-

tensities. Vibrational wavenumbers computed at DFT level have been adjudicated to be more reliable than those obtained by the computationally demanding Moller–Plesset perturbation methods. Finally, the calculated normal mode vibrational wavenumbers provide thermodynamic properties also through the principle of statistical mechanics. The assignments of the calculated wavenumbers supported by the animation option of chemcraft, a graphical interface for Gaussian programs, which gives a visual presentation of the shape of the vibrational modes.<sup>12</sup>

### 4. Results and discussion

#### 4.1 Geometric parameters

In this work, we performed full geometry optimization of the title compound. The optimized structure parameters of the title compound calculated by *ab*

**Table 1.** Selected bond lengths (Å) and inter-axial angles (°) for dacarbazine.

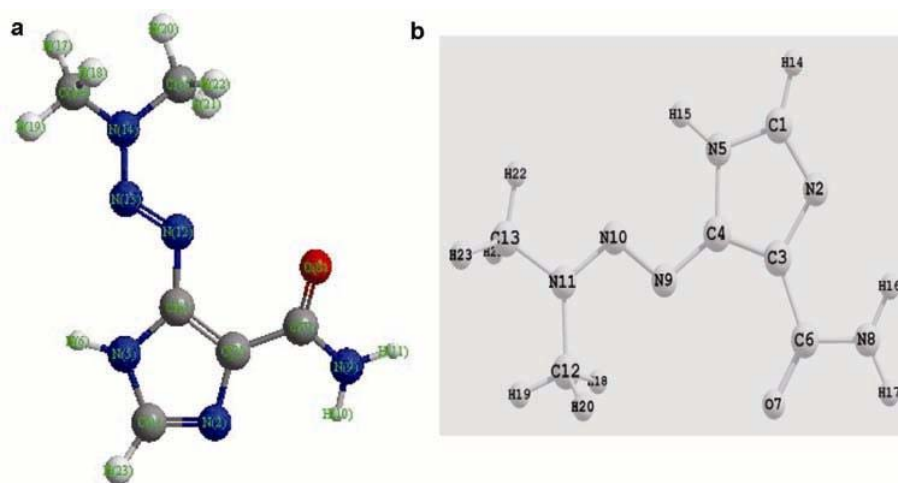
Molecular parameter	X-ray <sup>a</sup>	AM1	HF/6-31G	B3LYP/6-31G	B3LYP/6-311G	MP2/6-31G
<b>Bond length</b>						
C <sub>1</sub> -N <sub>2</sub>	1.330	1.349	1.297	1.326	1.325	1.260
C <sub>1</sub> -N <sub>5</sub>	1.380	1.396	1.365	1.378	1.376	1.266
C <sub>1</sub> -H <sub>14</sub>	1.080	1.095	1.064	1.077	1.074	1.100
C <sub>3</sub> -C <sub>4</sub>	1.390	1.428	1.365	1.392	1.389	1.346
C <sub>3</sub> -C <sub>6</sub>	1.470	1.480	1.467	1.473	1.472	1.351
N <sub>5</sub> -H <sub>15</sub>	0.990	0.986	0.990	1.008	1.005	1.009
C <sub>6</sub> -O <sub>7</sub>	1.230	1.247	1.231	1.254	1.254	1.208
C <sub>6</sub> -N <sub>8</sub>	1.380	1.376	1.351	1.369	1.367	1.369
N <sub>8</sub> -H <sub>16</sub>	0.990	0.988	0.991	1.009	1.006	1.012
N <sub>8</sub> -H <sub>17</sub>	0.990	0.989	0.991	1.007	1.004	1.012
N <sub>9</sub> -N <sub>10</sub>	1.250	1.250	1.248	1.298	1.299	1.248
N <sub>10</sub> -N <sub>11</sub>	1.340	1.335	1.310	1.338	1.339	1.352
N <sub>11</sub> -C <sub>12</sub>	1.470	1.460	1.455	1.465	1.464	1.438
N <sub>11</sub> -C <sub>13</sub>	1.460	1.460	1.448	1.456	1.456	1.438
C <sub>12</sub> -H <sub>18</sub>	1.100	1.123	1.081	1.095	1.091	1.113
C <sub>13</sub> -H <sub>22</sub>	1.100	1.121	1.078	1.090	1.086	1.113
C <sub>13</sub> -H <sub>23</sub>	1.100	1.122	1.083	1.097	1.092	1.113
CC		0.9944	0.9978	0.9994	0.9998	0.9965
MAD		0.0169	0.0197	0.0033	0.0197	0.1852
RMS		0.0204	0.0224	0.0045	0.0024	0.0036
<b>Bond angle</b>						
N <sub>2</sub> -C <sub>1</sub> -N <sub>5</sub>	110.450	111.935	110.594	110.874	110.844	111.004
N <sub>2</sub> -C <sub>1</sub> -H <sub>14</sub>	125.720	125.372	126.171	125.874	125.764	124.496
C <sub>1</sub> -N <sub>2</sub> -C <sub>3</sub>	107.080	106.138	107.005	106.479	106.453	103.997
N <sub>5</sub> -C <sub>1</sub> -H <sub>14</sub>	123.820	122.693	123.236	123.252	123.392	124.500
N <sub>2</sub> -C <sub>3</sub> -C <sub>6</sub>	121.390	124.281	120.437	120.372	120.14	123.593
C <sub>3</sub> -C <sub>4</sub> -N <sub>9</sub>	127.770	125.339	129.919	129.782	129.787	129.401
C <sub>3</sub> -C <sub>6</sub> -O <sub>7</sub>	123.570	122.386	123.365	123.856	123.927	119.997
N <sub>5</sub> -C <sub>4</sub> -N <sub>9</sub>	126.650	129.202	124.378	124.899	124.865	129.409
C <sub>4</sub> -N <sub>5</sub> -H <sub>15</sub>	125.460	126.296	124.607	123.420	123.384	120.001
C <sub>4</sub> -N <sub>9</sub> -N <sub>10</sub>	116.820	119.263	115.196	113.615	113.736	120.005
O <sub>7</sub> -C <sub>6</sub> -N <sub>8</sub>	120.700	120.185	122.341	122.897	122.706	120.000
C <sub>6</sub> -N <sub>8</sub> -H <sub>16</sub>	118.400	121.056	120.903	119.819	119.857	119.996
C <sub>6</sub> -N <sub>8</sub> -H <sub>17</sub>	117.280	118.547	118.551	118.832	118.764	120.003
N <sub>9</sub> -N <sub>10</sub> -N <sub>11</sub>	116.580	119.425	116.285	113.740	113.63	109.502
N <sub>10</sub> -N <sub>11</sub> -C <sub>12</sub>	122.300	123.978	120.858	121.131	120.988	109.446
N <sub>10</sub> -N <sub>11</sub> -C <sub>13</sub>	115.010	115.522	117.302	116.858	116.889	109.440
C <sub>12</sub> -N <sub>11</sub> -C <sub>13</sub>	117.780	113.380	121.840	122.010	122.123	109.506
N <sub>11</sub> -C <sub>12</sub> -H <sub>18</sub>	111.150	111.764	110.759	110.411	110.442	109.439
N <sub>11</sub> -C <sub>12</sub> -H <sub>19</sub>	108.370	108.144	107.953	108.283	108.295	109.457
N <sub>11</sub> -C <sub>13</sub> -H <sub>22</sub>	110.200	111.542	108.582	107.838	107.839	109.465
N <sub>11</sub> -C <sub>13</sub> -H <sub>23</sub>	110.150	107.023	110.822	111.002	111.031	109.447
H <sub>18</sub> -C <sub>12</sub> -H <sub>19</sub>	109.090	109.246	109.937	110.426	110.428	109.464
H <sub>22</sub> -C <sub>13</sub> -H <sub>23</sub>	108.560	108.733	108.906	109.124	109.067	109.202
CC		0.9715	0.9814	0.9751	0.9746	0.9568
MAD		1.3296	1.0395	1.3335	1.2750	1.3357
RMS		1.7229	1.4339	1.7452	1.6729	1.6150

<sup>a</sup>Geometrical parameters determined with X-ray diffraction method from ref. [6]

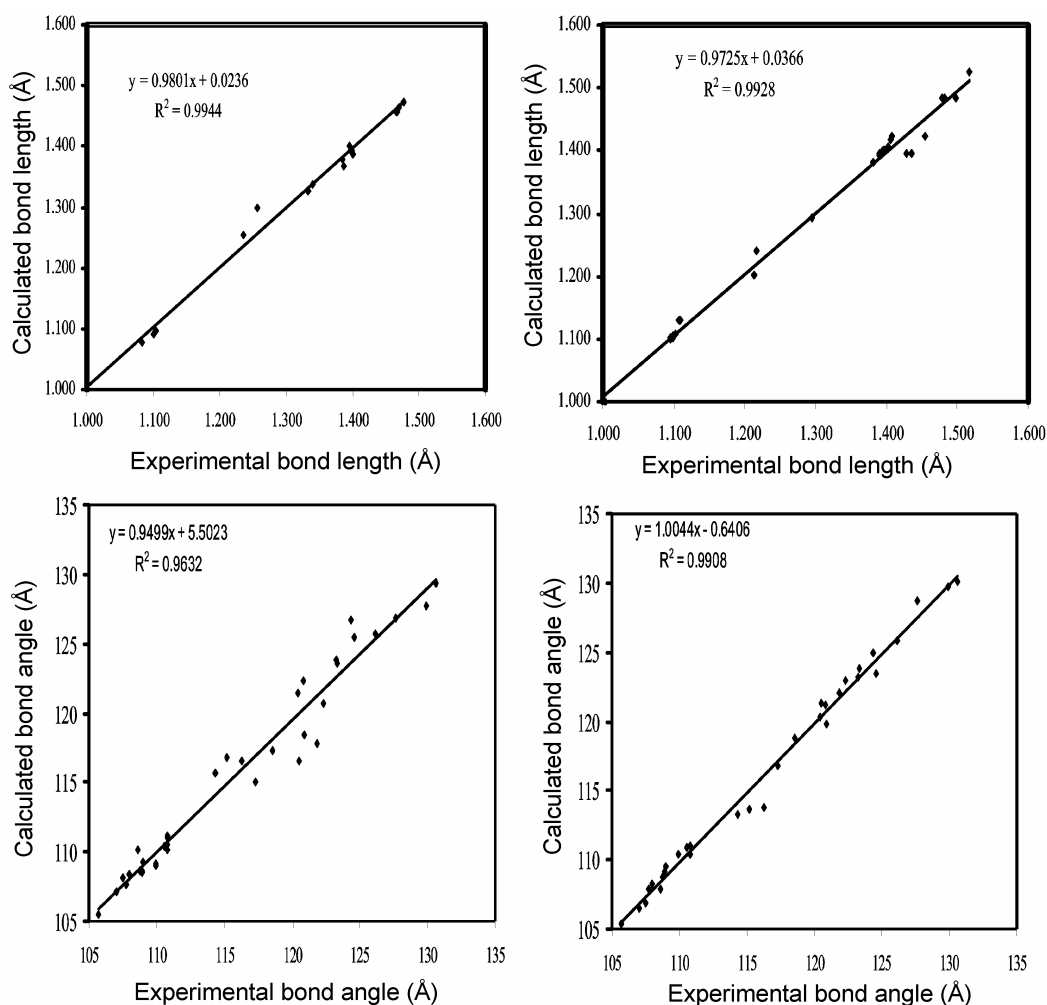
CC, Correlation coefficient; MAD, Mean arithmetic deviation; RMS, Root mean square error

*initio*, MP2, DFT and AM1 methods listed in table 1 are in accordance with atom numbering scheme given in figure 3b. The B3LYP method leads to ge-

ometry parameters, which are close to experimental data.<sup>6</sup> A statistical treatment of these data (see at the bottom of table 1) shows that for the bond lengths



**Figure 3.** a. X-ray structure of dacarbazine. b. Geometry of the dacarbazine optimized at B3LYP/6-31G(*d, p*).



**Figure 4.** Calculated bond lengths and bond angles in comparison with experimental data.

B3LYP/6-31G(*d, p*) (figure 4) is slightly better than the HF/6-31G(*d, p*) geometry. The correlation coefficient for bond lengths was 0.9994 for B3LYP/6-

31G(*d, p*) method. The agreement for bond angles is not as good as that for the bond distances. The slight variation with the experimental value is due to the

**Table 2.** Observed FTIR, FT-Raman and calculated wave numbers for dacarbazine using HF/6-31G(*d, p*), B3LYP/6-31G(*d, p*) and MP2/6-31G(*d, p*) methods.

Vibrational assignment	Calculated wave number (cm <sup>-1</sup> )							
	Observed wave number (cm <sup>-1</sup> )		HF 6-31G ( <i>d, p</i> )		B3LYP 6-31G ( <i>d, p</i> )		MP2 6-31G ( <i>d, p</i> )	
	FTIR	FT-Raman	Wave number	Rel Intensity	Wave number	Rel Intensity	Wave number	Rel Intensity
$\gamma_{as}NH_2$	3370 (w)	3371 (w)	3596	13	3376	8	3389	0
$\gamma NH$	3321 (w)		3544	17	3314	9	3380	38
$\gamma_s NH_2$	3232 (w)		3466	14	3238	8	3207	2
$\gamma_s CH$	2957 (w)	2937 (m)	3140	0	2978	0	3132	0
$\gamma_{as} CH_3$	2869 (w)		2994	2	2861	2	3129	0
$\gamma_{as} CH_3$	2853 (w)	2851 (w)	2988	3	2858	1	3124	5
$\gamma_{as} CH_2$	2819 (w)		2962	2	2814	1	3098	1
$\gamma_{as} CH_2$		2780 (w)	2930	6	2786	5	3092	2
$\gamma_s CH_3$	2755 (w)		2897	6	2756	5	2947	1
$\gamma_s CH_3$		2739 (w)	2877	13	2734	14	2943	4
$\gamma C=O$	1612 (s)	1613 (s)	1708	70	1620	80	1610	53
$\gamma C=N$	1510 (w)	1501 (m)	1673	57	1516	53	1572	11
$\rho C-NH_2$	1496 (s)		1657	11	1498	2	1509	1
$\rho NH_2$	1448 (w)	1441 (w)	1567	67	1434	6	1495	8
$\gamma ring CN$	1441 (w)		1549	8	1420	9	1490	1
$\gamma CC + \gamma ring + \rho NH_2$	1404 (m)	1402 (w)	1543	0	1406	1	1483	2
$\gamma CC + \alpha N - CH_2 + \beta NCH$	1394 (w)		1531	6	1395	8	1450	13
$\delta_{as} CH_3 + \gamma ring$	1383 (w)		1517	1	1386	2	1416	5
$\delta_{as} CH_3 + \gamma ring$		1386 (w)	1503	2	1386	6	1398	2
$\delta_{as} CH_3 + \gamma ring$		1369 (s)	1499	1	1364	3	1383	11
$\delta_s CH_3 + \gamma ring$	1337 (m)		1483	1	1345	4	1373	11
$\delta_s CH_3 + \gamma ring$	1295 (w)	1285 (w)	1456	16	1289	9	1245	48
$\delta_s CH_3 + \gamma ring + \beta NCH$	1280 (w)		1412	78	1282	100	1226	4
$\delta_s CH_3 + \gamma ring$		1263 (w)	1391	38	1266	1	1218	8
$\gamma CN + \delta CH$	1255 (w)		1382	29	1255	1	1191	5
$\gamma ring + \delta CH$	1209 (w)		1342	9	1223	2	1139	15
$\alpha NH + \gamma NNN$		1166 (w)	1273	3	1166	1	1131	1
$\gamma NN + \delta CH_3$	1137 (w)	1121 (w)	1223	4	1130	4	1106	0
$\gamma NN + \beta CH$	1082 (s)	1078 (w)	1184	1	1087	0	1074	18
$\beta CH + \delta CNC$		1064 (w)	1166	1	1067	0	1061	14
$\rho CH_2 + \beta CH$	1052 (w)		1145	0	1047	0	1040	2
$\rho C-NH_2 + \delta CNC$	1022 (s)	1028 (w)	1132	24	1027	8	996	1
$\rho CH_2 + \delta CNC$	966 (w)		1113	7	1026	8	987	1
$\rho CH_3 + \beta CH$	930 (s)	950 (w)	1086	3	999	18	974	19
$\rho CH_3 + \gamma ring$	889 (m)	889 (w)	1085	42	995	11	954	26
$\Delta ring + \gamma ring (CN)$	874 (w)	876 (w)	977	4	891	3	841	1
$\gamma N-CH_3 + \alpha NNN$	830 (w)	844 (w)	917	0	841	2	811	8
$\beta NCH + \beta NCC$	794 (w)	797 (m)	915	3	774	1	767	100
$\beta CH$	745 (w)	743 (w)	857	14	748	4	726	9
$\gamma NN + \gamma N-CH_3 + \alpha CNC$	718 (w)		788	0	735	0	698	18
$\beta NH + \beta CCO$	682 (w)	670 (w)	759	2	665	4	638	14
$\beta (CCN + NH)$	630 (m)	631 (m)	718	65	643	22	598	6
$\alpha NNN + \alpha CNC$	625 (w)		690	7	635	18	548	2
$\beta NCO + \beta NH + \beta CH$	622 (w)	610 (w)	690	4	635	2	589	8
$\tau C-NH_2 + \beta NH_2$	593 (w)		629	19	594	13	493	15
$\rho NH_2 + \alpha NNH + \alpha CCO$	554 (w)	560 (m)	605	8	557	6	474	2
Ring deformation	525 (w)		578	10	525	3	463	30
$\beta NH + \alpha NCH$	514 (w)	510 (w)	564	3	512	23	407	8
$\alpha C-NH_2$		420 (w)	441	2	410	2	369	4

(contd...)

**Table 2.** (contd...)

Vibrational assignment	Observed wave number (cm <sup>-1</sup> )		Calculated wave number (cm <sup>-1</sup> )					
			HF 6-31G (d, p)		B3LYP 6-31G (d, p)		MP2 6-31G (d, p)	
	FTIR	FT-Raman	Wave number	Rel Intensity	Wave number	Rel Intensity	Wave number	Rel Intensity
ringCNH + $\rho$ NH <sub>2</sub> + $\beta$ NCO		381 (m)	415	0	383	0	349	9
$\alpha$ NNH + $\alpha$ CCO			413	2	369	0	325	8
$\omega$ NH <sub>2</sub>		337 (m)	393	0	361	1	285	3
$\Omega$ CH <sub>3</sub> $\alpha$ CNH		285 (w)	315	2	292	2	256	3
$\beta$ C-NH <sub>2</sub>		226 (m)	272	0	253	0	243	2
$\beta$ CNH + $\beta$ CH <sub>2</sub>			225	1	204	1	206	2
$\alpha$ NCO + $\beta$ NH <sub>2</sub>			202	3	181	2	188	1
$\tau$ CH <sub>2</sub> + $\tau$ CH <sub>3</sub>			188	1	174	1	159	2
$\tau$ CH <sub>3</sub> + $\beta$ NNN + $\beta$ NCH + $\beta$ NH <sub>2</sub>		126 (w)	146	0	142	0	155	2
Lattice vibrations			113	0	98	0	144	2
$\beta$ NCO + $\omega$ CH <sub>3</sub>			78	1	71	1	90	0
$\omega$ CH <sub>3</sub>			63	0	58	2	63	1
$\omega$ CH <sub>3</sub>			56	2	47	0	46	1
$\omega$ CH <sub>3</sub>			38	0	23	0	36	0

fact that the optimization performed in an isolated condition, whereas the crystal environment affected the experimental X-ray structure.

#### 4.2 Vibrational assignments

The FT-IR and FT-Raman spectra of the title compound were shown in figures 1–2. None of the predicted vibrational spectra have any imaginary frequency, implying that the optimized geometry is located at the local lowest point on the potential energy surface. We know that *ab initio*, MP2 and DFT potentials systematically overestimate the vibrational wave numbers. These discrepancies corrected either by computing anharmonic corrections explicitly or by introducing a scaled field<sup>13</sup> or directly scaling the calculated wave numbers with the proper factor.<sup>14</sup> Considering systematic errors with scaling factor of 0.9051, 0.9500, and 0.9679, we calibrated the vibrational wave numbers calculated by HF, MP2, and B3LYP, respectively. After scaled with a scaling factor, the deviation from experiments is less than 10 cm<sup>-1</sup> with a few exceptions. Theoretical and experimental results of the title compound are shown in table 2. The DFT method is superior to HF and MP2 methods in terms of realistic reproduction of both band intensity distribution and general spectral features.

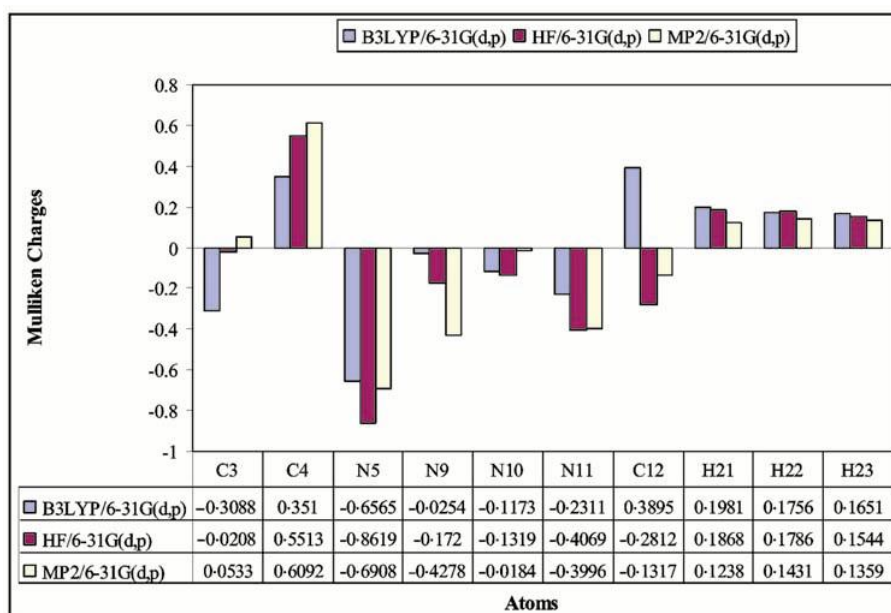
**4.2a C–O vibration:** The characteristics infrared absorption frequencies of carbonyl group in ketones

are normally strong in intensity and found in the region 1685–1660 cm<sup>-1</sup>. The carbon–oxygen double bond formed by  $p_{\pi}$ – $p_{\pi}$  between carbon and oxygen. Because of the different electro negativities of carbon and oxygen atoms, the bonding electrons not equally distributed between the two atoms. The lone pair of electrons on oxygen also determines the nature of the carbonyl group.<sup>15</sup> The CO stretching vibration in dacarbazine has a scaled computed frequency of 1620 cm<sup>-1</sup>. This is in agreement with strong experimental frequency in FT-IR spectrum at 1612 cm<sup>-1</sup>. The C–O out-of-plane bending vibration mode with the theoretical frequency of 142 cm<sup>-1</sup> agrees well with experimental FT-Raman value. The above conclusions are in agreement with literature value.<sup>16</sup>

**4.2b C–NH<sub>2</sub> vibrations:** The molecule under investigation possesses only one NH<sub>2</sub> group and hence one expects one symmetric and one asymmetric N–H stretching vibrations in NH<sub>2</sub> group. In all the primary aromatic amines, the N–H stretching frequency occurs in the region 3300–3500 cm<sup>-1</sup>.<sup>17</sup> Hence, the weak bands in IR spectrum were located at 3370 and 3232 cm<sup>-1</sup> assigned to N–H asymmetric and symmetric stretching vibrations, respectively in NH<sub>2</sub> group. These assignments agree well with the earlier reports.<sup>18</sup> The scaled –NH<sub>2</sub> asymmetric and symmetric stretching are in the range of 3376–3238 cm<sup>-1</sup> in B3LYP/6-31G (d, p). The computed –NH<sub>2</sub> scissoring vibration at 1498 cm<sup>-1</sup> in B3LYP/6-31G(d, p) is in agreement with the expected experimental value at

**Table 3.** Mulliken atomic charges of dactarbazine for different levels and basis sets.

Atom with numbering	B3LYP			HF	MP2
	6-31G*	6-311G( <i>d, p</i> )	6-31G( <i>d, p</i> )	6-31G( <i>d, p</i> )	6-31G( <i>d, p</i> )
C <sub>1</sub>	0.2301	0.2322	0.1718	0.2941	0.3488
N <sub>2</sub>	-0.4117	-0.4096	-0.2461	-0.4753	-0.6033
C <sub>3</sub>	-0.1242	-0.1221	-0.3088	-0.0208	0.0533
C <sub>4</sub>	0.4759	0.4780	0.3510	0.5513	0.6092
N <sub>5</sub>	-0.7332	-0.7311	-0.6565	-0.8619	-0.6908
C <sub>6</sub>	0.5961	0.5982	0.6378	0.7439	0.7671
O <sub>7</sub>	-0.4137	-0.4116	-0.3642	-0.5735	-0.6408
N <sub>8</sub>	-0.7863	-0.7842	-0.8015	-0.9632	-0.7656
N <sub>9</sub>	-0.2519	-0.2498	-0.0254	-0.1720	-0.4278
N <sub>10</sub>	-0.0217	-0.0196	-0.1173	-0.1319	-0.0184
N <sub>11</sub>	-0.3670	-0.3649	-0.2311	-0.4069	-0.3996
C <sub>12</sub>	-0.3103	-0.3082	0.3895	-0.2812	-0.1317
C <sub>13</sub>	-0.3240	-0.3219	-0.3481	-0.2484	-0.1223
H <sub>14</sub>	0.2037	0.2058	0.1968	0.2524	0.1776
H <sub>15</sub>	0.3548	0.3569	0.3686	0.4468	0.3440
H <sub>16</sub>	0.3446	0.3467	0.3274	0.3954	0.3377
H <sub>17</sub>	0.3267	0.3288	0.3240	0.3832	0.3128
H <sub>18</sub>	0.2254	0.2275	0.2132	0.2055	0.1429
H <sub>19</sub>	0.1710	0.1731	0.1647	0.1507	0.1821
H <sub>20</sub>	0.2254	0.2275	0.1944	0.1920	0.1220
H <sub>21</sub>	0.1973	0.1994	0.1981	0.1868	0.1238
H <sub>22</sub>	0.1958	0.1979	0.1756	0.1786	0.1431
H <sub>23</sub>	0.1973	0.1994	0.1651	0.1544	0.1359

**Figure 5.** Comparison of different methods for calculated atomic charges.

1496  $\text{cm}^{-1}$ . The C–NH<sub>2</sub> out-of-plane and in-plane-bending vibrations at 226 and 381  $\text{cm}^{-1}$  observed at FT-Raman spectrum agree well with theoretically obtained values using B3LYP/6-31G(*d, p*).<sup>19</sup>

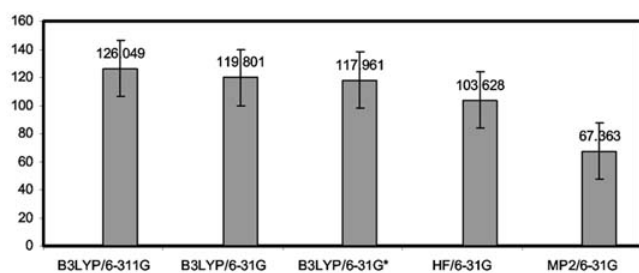
4.2c C=N, C–N vibrations: The identification of C–N vibrations is a difficult task, since the mixing of vibrations is possible in this region. However, with the help of the animation option of chemcraft

**Table 4.** Calculated polarizabilities for dacarbazine.

Basis set	$\alpha_{xx}$	$\alpha_{xy}$	$\alpha_{yy}$	$\alpha_{xz}$	$\alpha_{yz}$	$\alpha_{zz}$	$\langle\alpha\rangle$
B3LYP/6-311G	204.182	-10.604	118.330	-0.002	0.003	55.637	126.049
B3LYP/6-31G	198.371	-11.117	113.912	0.001	0.000	47.120	119.801
B3LYP/6-31G*	193.266	9.551	107.098	3.308	1.633	53.520	117.961
HF/6-31G	164.977	6.405	100.136	-0.002	-0.002	45.773	103.628
MP2/6-31G	106.556	5.545	73.206	2.706	1.950	23.133	67.363

**Table 5.** Comparison of HOMO, LUMO, energy gaps ( $\Delta\varepsilon_{\text{HOMO-LUMO}}$ ), first ionization potentials and chemical hardness of dacarbazine (eV).

Basis set	$\varepsilon_{\text{HOMO}}$	$\varepsilon_{\text{LUMO}}$	1st ionization potential	( $\Delta\varepsilon_{\text{HOMO-LUMO}}$ )	Chemical hardness
B3LYP/6-311G	-518.706	-1.684	-260.195	517.021	258.510
B3LYP/6-31G	-519.302	-1.477	-260.382	517.825	258.915
B3LYP/6-31G*	-518.952	-1.615	-260.283	517.337	258.668
HF/6-31G	-557.848	2.497	-280.172	555.351	277.675
MP2/6-31G	-512.650	-1.586	-257.118	511.064	255.532

**Figure 6.** Comparison of different methods for calculated polarizabilities.

graphical interface for Gaussian programs the C–N vibrations identified. Silverstein<sup>20</sup> assigned C–N stretching absorption in the region 1382–1266  $\text{cm}^{-1}$  for aromatic amines. The IR bands appearing at 1510 and 1441  $\text{cm}^{-1}$  are assigned to  $\nu_{\text{C=N}}$  vibrations and 1255 and 1209  $\text{cm}^{-1}$  are assigned to  $\nu_{\text{C-N}}$  vibrations with the  $\delta_{\text{CH}}$  for the title compound. All these results agree with the results of Shanmugam *et al.*<sup>21</sup> and Sundaraganesan *et al.*<sup>22</sup>

**4.2d Methyl group vibrations:** The title compound dacarbazine, possesses two  $\text{CH}_3$  groups attached to the side chain of N=N–N to the five member ring. There are nine fundamentals one can expect to each  $\text{CH}_3$  group, namely the symmetrical stretching in  $\text{CH}_3$  ( $\text{CH}_3$  sym. stretch) and asymmetrical stretching (in plane hydrogen stretching mode); the symmetrical ( $\text{CH}_3$  sym. deform) and asymmetrical ( $\text{CH}_3$  asym. deform) deformation modes; the in-plane rocking,

out-of-plane rocking, twisting and bending modes. For the methyl compounds, the stretching mode appears in the range of 2825–2870  $\text{cm}^{-1}$ , lower in magnitude compared to its value in  $\text{CH}_3$  compounds (2860–2935  $\text{cm}^{-1}$ ), whereas the two asymmetric modes for both the types of compounds lie in the same region of 2925–2985  $\text{cm}^{-1}$ . The FTIR bands at 2869 and 2755  $\text{cm}^{-1}$  and FT-Raman band at 2851 and 2739  $\text{cm}^{-1}$  represent the asymmetric and symmetric  $\text{CH}_3$  stretching vibrations of the methyl group of dacarbazine.

## 5. Other molecular properties

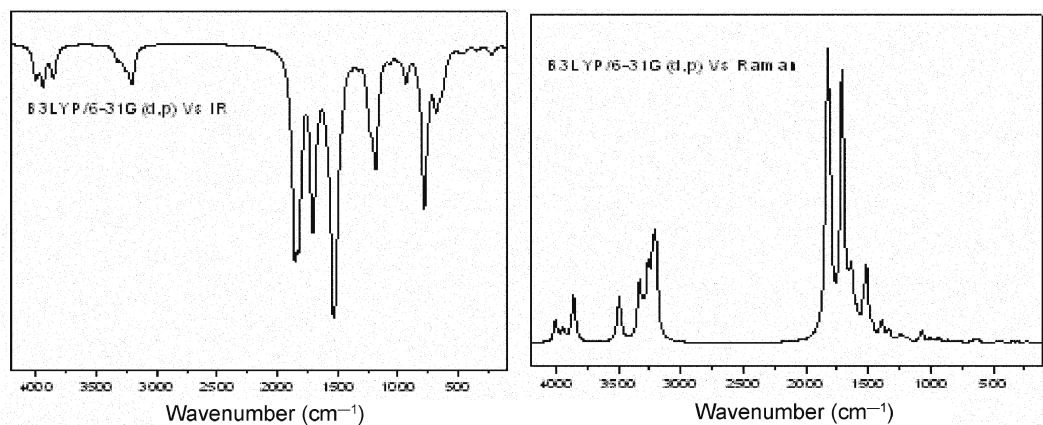
### 5.1 Mulliken charges

The calculation of effective atomic charges plays an important role in the application of quantum mechanical calculations to molecular systems. Our interest here is in the comparison of different methods to describe the electron distribution in dacarbazine as broadly as possible, and assess the sensitivity of the calculated charges to changes in (i) the choice of the basis set; (ii) the choice of the quantum mechanical method. Mulliken charges, calculated by determining the electron population of each atom as defined in the basis functions. The Mulliken charges calculated different levels and at different basis sets listed in table 3. The results can, however, better be represented in graphical form as has been given in figure 5. From these results, it will be possible to



**Table 6.** Theoretically computed energies (a.u.) zero-point vibrational energies (kcal mol<sup>-1</sup>), rotational constants (GHz), entropies (cal mol<sup>-1</sup> K<sup>-1</sup>) and dipole moment (*D*) for dacarbazine.

Parameters	AM1	HF	B3LYP		MP2
		6-31G( <i>d, p</i> )	6-31G( <i>d, p</i> )	6-311G ( <i>d, p</i> )	6-31G( <i>d, p</i> )
Total energy		-634.00265	-638.07212	-638.11876	-638.04222
Zero-point energy	115.1	124.0	118.3	113.8	116.7
Rotational constants		1.4787	1.5202	1.4550	1.6342
		0.4718	0.5007	0.4623	0.5007
		0.3592	0.3943	0.3524	0.3941
Entropy					
Total	104.119	111.227	101.527	115.254	92.527
Translational	41.355	41.561	41.505	41.505	41.505
Rotational	31.562	31.528	31.277	31.584	31.277
Vibrational	31.207	36.279	29.745	42.166	19.745
Dipole moment	-	6.455	5.962	5.998	5.965

**Figure 7.** Computed spectra of dacarbazine at B3LYP/6-31G(*d, p*).

say to the change to charge distribution by a change in basis set. The charges depending on basis set and are changed due to polarization.

## 5.2 Molecular polarizability

We have investigated the effect of the basis set on molecular polarizability of dacarbazine using Gaussian 03W. In this study, the computation of molecular polarizability of dacarbazine with different basis sets reported. Here,  $\alpha$  is a second rank tensor property called the dipole polarizability and mean polarizability  $\langle\alpha\rangle$  are evaluated using

$$\langle\alpha\rangle = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}). \quad (1)$$

The polarizability calculations carried out for different basis sets of dacarbazine are summarized in table 4. As seen from the figure 6, the largest polarizability was observed for B3LYP/6-311G (*d, p*).

## 5.3 HOMO-LUMO energy gaps and ionization potentials

According to Koopmans' theorem,  $I = -E_{\text{HOMO}}$ ,  $A = -E_{\text{LUMO}}$ . The ionization potentials and affinity potentials from Koopmans' theorem (or the HOMO and LUMO energies) for dacarbazine are summarized in table 5. The substitutional perturbation affects both the HOMO orbital and LUMO orbital for dacarbazine. In general, the HOMO orbital becomes less bound while the LUMO more bound with increasing heat of formation. From table 5, the lowest energy gap found at MP2 method.

## 5.4 Thermodynamic properties

The calculated thermodynamic parameters are presented in table 6. Scale factors have been recommended<sup>23</sup> for an accurate prediction in determining the zero-point vibrational energies and the entropy

S. The variation in the ZPVEs seems to be insignificant. The total energies found to decrease with increase of the basis sets. The changes in the total entropy of dacarbazine at room temperature at different basis sets are only marginal.

## 6. Conclusion

The results of the study lead to the following conclusions: (i) The frequency assignments performed for the first time from FTIR and FT-Raman spectra recorded were for dacarbazine. Theoretical DFT and *ab initio* calculations of the vibrational spectra of the molecule presented in this paper were compared with the FTIR and Raman spectra. (ii) Geometries reported within the limits of accuracy of available experimental data. The molecular geometry of dacarbazine was best at the B3LYP level of DFT. (iii) Mulliken charges of dacarbazine at different levels were calculated and the results discussed. (iv) Molecular polarizability and ionization potential of dacarbazine were discussed and reported.

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