

DIPOLE MOMENT OF NITROGEN DIOXIDE AND DINITROGEN DIOXIDE—THE STRUCTURE OF THE DIMER

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THERE have been numerous studies on the properties of these compounds and there have been reviews of these^{11,1,12} but one property that appeared to be out of tune with the accepted structure of the dimer is the dielectric constant.¹⁷ It appeared worthwhile studying this aspect further. A difficulty in the measurements is the ease with which nitrogen dioxide and the dimer form complexes with a variety of otherwise desirable solvents for these studies. Our measurements have therefore been confined to solvents with available pi-orbital electrons and to non-donor solvents which are non-aromatic.

EXPERIMENTAL

Solvents.—Benzene was purified by standard methods of chemical treatment and fractional crystallisation, distilled over sodium, allowed to stand over sodium partially melted and the residue then stored over sodium.

p-Xylene was purified by similar methods and fractional crystallisation to constant freezing point was adopted for the final purification.

Carbon tetrachloride was purified as in earlier studies from these laboratories and stored over sticks of potassium hydroxide. Phosphorus pentoxide was unsuitable as drying agent and we confirm the observations of Smith and Witten²¹ on this.

Cyclohexane was purified by the method of Gillam and Stern⁹, washed free from acid, treated with dilute permanganate, dried first over calcium chloride and then over sodium and fractionated.⁸ Liquid dinitrogen tetroxide was prepared from lead nitrate, freed from dissolved oxygen by repeated low pressure distillation¹² and stored in sealed tubes. For use, the liquid was slowly vapourised in a closed system through a phosphorus pentoxide trap and absorbed in a weighed quantity of the solvent.

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Table I gives the characteristics of the solvents used in the studies.

TABLE I
Physical properties of solvents used at 305° K.

Solvent	B.P./M.P. ° C. at 760 mm.	d_4^{32}	n_D^{32}	ϵ^{32}	U.V. cut off m μ	1 cm. quartz cell
Benzene	80.10/ 5.50	0.86521	1.4934	2.2588	280	..
<i>p</i> -Xylene	138.4 /13.3	0.85068	1.4914	2.2525	270	..
Carbon Tetra- chloride	76.8/ ..	1.57060	1.4536	2.2155	265	..
Cyclohexane	80.7 / 6.5	0.76760	1.4220	2.0040	230	..

Dielectric constant measurements were made by a heterodyne beat method, the solutions being kept in a modified Sayce Briscoe cell.²⁰ Guggenheim's procedure was adopted in evaluating the dipole moments, the method of Harris and Bush also being used for comparison of the two. The values for the monomer and dimer were computed using data for equilibrium constant for the system and the known enthalpy for the dimerisation reaction so as to get the values at the temperature of measurement. Typical experimental results are presented in Tables II and III.

DISCUSSION OF RESULTS

Two aspects of the problem need elucidation. We can consider the variation with solvents first. Addison and coworkers have made an extensive study of the different solutions of dinitrogen tetroxide.² Among the non-donor non-aromatic systems, they consider that the dipolar character of the C-Cl bond should lead to dipolar interaction unlike the hydrocarbon system using cyclohexane. This would require a dipole moment of N₂O₄ which is higher in carbon tetrachloride. Also an increase in the dielectric constant of the solvent should show a trend in the same direction of the dipole moment also.¹⁰ We find that the dipole moment in cyclohexane is distinctly higher than in carbon tetrachloride. This could arise from a possible change in the solvent. Le Fevre¹⁴ has shown that at higher temperatures cyclohexane contains more of the axial isomers which is reflected also in the density and refractive index. It is significant that in this solvent dielectric constant is less than the square of the refractive index, while in

TABLE II

Experimental data on measurements with NO₂, N₂O₄ mixtures

Solvent	Weight fraction of solute × 10 ⁵	$\epsilon \times 10^4$	$n^2 \times 10^4$	α extra-polated from ϵ	ν extra-polated from n_D
Benzene	540	22610	22330	0.91	0.55
	1075	22670	22350		
	2156	22782	22370		
	4314	22973	22380		
<i>p</i> -Xylene	750	22595	22270	0.92	0.55
	1510	22660	22290		
	3021	22800	22300		
	4500	22930	22310		
Carbon Tetrachloride	1250	22235	21160	0.89	0.54
	1750	22305	21180		
	2500	22370	21200		
	3500	22460	21210		
Cyclohexane	750	20080	20240	0.80	0.55
	1250	20125	20250		
	2500	20235	20270		
	3750	20340	20280		

TABLE III

Dipole moments of NO₂ and N₂O₄ in Debye Units

Solvent	NO ₂		N ₂ O ₄	
	Guggenheim's method	Harris and Brush's method	Guggenheim's method	Harris and Brush's method
Benzene ..	0.38	0.41	0.54	0.58
P-Xylene ..	0.41	0.44	0.57	0.62
Carbon Tetrachloride	0.29	0.31	0.41	0.44
Cyclohexane ..	0.37	0.39	0.53	0.56

the other solvents the reverse is the case. Part of the observed effect also arises from the interaction between the C-H and N-O dipoles of solvent and solute. Our measurements differ also in the use of a composition which should be richer in the monomer. A factor not to be ignored is the possibility of ionic forms of the dimer as is shown by the corrosion of the silver film of the cell.

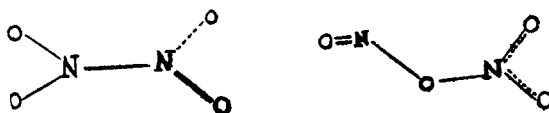
In the carbon tetrachloride solutions, apart from dipole interaction, one cannot ignore exchange forces. Pi-bonding between autocomplexes of N_2O_4 and the 3-*d* orbitals of the chlorine of CCl_4 ¹⁶ are not impossible. The existence of electronic interactions between N_2O_4 and benzene is shown by the strongly coloured solutions invariably obtained by us. Addison and Sheldon² as also Szabe²⁴ shake the solvent with liquid N_2O_4 and have reported an absence of colour while our observations are more analogous to Mullikan's charge transfer bonding forces observed with solutions of iodine.¹⁶ The colour of *p*-xylene solutions are similar to that of 2-nitro *p*-xylene where we have indications of interaction between the methyl hydrogen atoms and the nitro group.¹⁸ The higher moments observed in the donor solvents compared to the non-donor solvents is also consistent with a picture of overlap orbitals between the pi-electrons of solvent and those of the dimer.

Even allowing for changes in polarisation through solvent solute interactions, it is clear that both monomer and dimer have a definite moment with N_2O_4 having a higher moment than NO_2 . This clearly rules out any structure of N_2O_4 which is symmetric and planar. The uncertainty in the values of atom polarisation which can be large in this molecule cannot by itself be adequate. Chemical evidence which has been thoroughly discussed^{1, 11} is not conclusive, as it is not possible to rule out rearrangement during reaction. We are thus forced to consider essentially physical evidence in understanding the structure. As Bent has indicated⁵ several conformations are possible in structure both with and without a N-N bond.

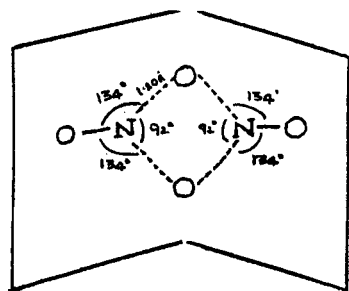
Most discussions of the structure of this molecule do not appear to take note of some factors. Dissociation into NO_2 involves an activation energy of 13 K. cal^{7, 4} and from the data, an entropy of activation of about 14 entropy units can be calculated. The N-N bond distance of 1.75° is much longer than for a single bond and cannot account for such an activation energy. Electron Spin Resonance studies of Atkins and his associates³ have shown that when compared with carbon in CO_2 , there is less localisation of unpaired electrons on nitrogen in NO_2 . This has been interpreted in these terms: "Thus the greater delocalisation of the unpaired elec-

tron in NO_2 will oppose dimerisation which occurs through bonding between nitrogen atoms".²³ The conclusion is clearly based on the assumed planar structure of the dimer. Is this necessary?

Apart from the definite dipole moment two other observations confirm a non-symmetrical structure. Snyder and Hirsatsune²² have reported that the energy barrier to free rotation about the N-N axis is about 2.9 K. cal. while Bernstein and Burns had earlier reported 8.5 K. cal.^{5a} which compares with 4 K. cal. noticed with H_2O_2 about the O-O axis.¹³ The number of coincidences between infra-red and Raman vibrations reported by Wiener and Nixon²⁵ suggests also an unsymmetrical structure. It is quite possible that the position is quite complicated and the system may contain a proportion of the symmetrical structure too but in the main, one has to consider the following alternatives:



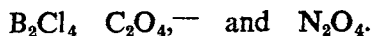
(a) N-O-O planes perpendicular to each other. (b) Several conformers possible.



(c)

The bridge structure was first suggested by Longuet-Higgins but has not found favour on physical grounds. The change from a planar to a non-planar arrangement of the type indicated (Fig. 1 c) is more in conformity with all the properties including dipole moment. The planar structure initially supported by the crystallographic studies of Robertson⁶ places the solid structure as different from the gas structure indicated by electron diffraction.¹⁹ Spectroscopic evidence is not unequivocal and even in the frozen state Bent⁵ has shown the need for several structures including unsymmetrical ones. Coulson's suggestion^{7a} of a π only bond between the nitrogen atoms needs a re-examination.

A point that has been urged in favour of the symmetrical structure with a N-N bond is a comparison of the isoelectronic systems



The first compound having a longer B-B bond has been shown by Mann and Fane¹⁵ to be non-planar in the liquid and gas states (V_d symmetry) while the oxalate ion is planar but with a *shortened* C-C bond. Instead of the far-fetched interpretation of the ESR studies in favour of a N-N bond, it is simpler to consider the results as an indication of a non-planar bridge structure. This in its turn will require a re-examination of the spectral data. An oxygen bridge of this type indicated (Fig. 1 *c*) can account readily for the dimerisation of NO_2 through the use of the orbitals localised on the oxygen. The larger O-N-O angle and N-N bond distance also follow readily. It is quite possible that N-O bond in the bridge is somewhat longer by about 0.08 Å.

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