

Structure of isopropyl-*N*-phenyl carbamate—a plant hormone

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Abstract. The structure of isopropyl-*N*-phenylcarbamate was solved by direct methods and refined to an *R* of 0.123 for 455 observed reflections. The molecule is stabilised by N-H . . . O hydrogen bonds (2.873 Å). The angle between the phenyl ring and the carbamate group is 31(4)°. Charge density calculations were carried out on this molecule using the Huckel LCAO-MO method for π charges and the DelRe method for σ charges. The charge separation between the ring atom with a net positive charge and the tail methyl group carbons are 5.53 and 5.83 Å.

Keywords. Plant hormone; isopropyl-*N*-phenylcarbamate; carbamate activity.

1. Introduction

The structure of isopropyl-*N*-phenyl carbamate (IPC) was determined as part of a project on plant hormones. IPC is an effective plant growth inhibitor and hence a selective herbicide. It is an isopropyl ester of carbamic acid having antipyretic property, is an inhibitor of photosynthesis and is known to have sedative and hypnotic properties like urethane (an aryl ester of carbamic acid) (Crafts and Robbins 1962). Carbamic acid esters are very active against certain grasses (Templeman *et al* 1945). Usually it is applied to the soil as there should be intimate mixing of the chemical with the soil to bring about injury to the rhizomes (Freed 1951).

Crystal structures of several carbamates, urethane (Bracher and Small 1967), 2-propylpentyl carbamate (DPEC), 4-propylheptyl *N*-phenyl carbamate (DPBC), (Cohen *et al* 1977), ammonium carbamate (Adams and Small 1973). Isomethyl *p*-bromophenyl carbamate (Kartha *et al* 1976), isopropyl-*N* (methyl furoxan) carbamates (INMF) (Calleri *et al* 1977) etc. have been determined in the past. The results from the present study are compared with the earlier one.

2. Experimental

IPC is soluble in *n*-propyl alcohol and on slow evaporation thin needle shaped crystals of the size 0.5 × 0.3 × 0.1 mm are obtained. Its structure and other parameters are: C₁₀H₁₃NO₂; Orthorhombic; *Pca*2₁; *a* = 9.006(6); *b* = 11.788(7); *c* = 9.726(6); *V* = 1042 Å³; *z* = 4; *D_c* = 1.15; *D_m* = 1.13(2) mg m⁻³; *Mr* = 179.2; Melting point = 84°C; $\lambda(\text{CoK}\alpha)$ = 1.7903 Å. As IPC is unstable and sublimes, the crystal was sealed in a lindemann capillary and the space group was uniquely determined to be

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Pca₂, from systematic absences. The crystal was mounted on Picker FACS-I four circle diffractometer and the accurate cell parameters were obtained by the least squares fit (Main and Woolfson 1963) for the settings of 21 reflections in the $\pm 2\theta$ values.

The three-dimensional intensity were measured with the Fe filtered CoK α ($\lambda = 1.793 \text{ \AA}$) radiation in the $\theta - 2\theta$ mode for $2\theta \leq 130^\circ$ at a scan rate of 2° min^{-1} . The scan range was 2° and the back grounds were measured for 10 sec each. The intensities were corrected for Lorentz and polarization effects and no absorption correction was applied ($\mu(\text{CoK}\alpha) = 1.7082 \text{ cm}^{-1}$, $|F_o| > 2\sigma(F)$) were considered observed.

As the compound was volatile, the quality of data collected were poor and this restricted the accuracy of the results obtained. Nevertheless, due to its importance as a herbicide the conformational analysis was carried out to compare the structure activity of IPC with other plant hormones.

The structure was solved using the program MULTAN (Main *et al* 1980). 163 reflections with $E > 1.2$ were used in phase propagation. The initial R factor for the model came out to be 0.338. After successive block diagonal least squares refinement (Shiono 1968) of the non-hydrogen atoms, with isotropic temperature factors, the reliability index dropped to 0.177. Further cycles of block-diagonal least squares refinement with anisotropic thermal parameters for all non-hydrogen atoms, isotropic temperature factors for hydrogen atoms (from geometry and ΔF synthesis) and Hughes weighting scheme (Hughes 1941)

$$W = 1/F_{\min}^2 \quad \text{for } |F_o| < F_{\min} \quad \text{and} \quad W = 1/|F_o|^2 \quad \text{for } |F_o| \geq F_{\min},$$

where $F_{0\min} = 12$ brought down the R -index to 0.127. Two cycles of full matrix least squares refinement using the program LALS (Gantzel *et al* 1961) gave a final R value of 0.123. The hydrogens were assigned isotropic temperature factors of the atoms to which they were bonded and included in the structure factor only and were not refined. Atomic scattering factors for the C, N and O were taken from the International tables (1962) and for the hydrogens from (Stewart 1965).

3. Discussion

The positional parameters are listed in table 1 and the bond length and bond angles are given in table 2. Figure 1 depicts the packing of the molecule down the a -axis. The molecule is in all *trans*-confirmation with C(8)-N(7)-C(5)-O(4) and N(7)-C(5)-O(4)-C(2) torsion angles $-170(3)^\circ$ and $-175(3)^\circ$ respectively. The molecule is stabilized by N-H . . . O type hydrogen bonds [$2.87(4)\text{\AA}$]. The NH . . . O(6) distance is 2.09 \AA and N(7)-H . . . O(6) angle is $158(3)^\circ$.

The bond distances C(12)-C(13) ($1.48(3)$), C(1)-C(2) ($1.59(5)$) and C(2)-C(3) ($1.23(5)$) deviate from standard values. However only C(2)-C(3) deviation is significant, at 6σ level. This shortening of the bond may be due to the fact that the atom C(3) has a very large thermal vibration. The carbamate group dimensions (table 2) viz., C(5)-N(7) ($1.42(6)$), C(5)-O(6) ($1.19(6)$) and C(5)-O(4) ($1.32(6)$) compare well, within the experimental errors, with the values observed in isomethyl-*p*-bromophenyl carbamate (Kantha 1976), isopropyl-*N* (methyl-furoxen) carbamate (Calleri *et al* 1977) and with other carboxylic acid esters rather than the amides (Bracher and Small 1967).

Table 4 lists the conformational parameters of some carbamates. The benzene ring and the carbamate group are planar within experimental error. The angle between these

Table 1a. Positional parameters of non-hydrogen atoms with e.s.d.'s in parenthesis.

Atom	x	y	z
C1	-0.172 (3)	0.152 (2)	0.397 (3)
C2	-0.038 (4)	0.126 (5)	0.300 (4)
C3	-0.042 (2)	0.032 (2)	0.241 (3)
O4	0.085 (2)	0.171 (2)	0.372 (4)
C5	0.186 (4)	0.218 (5)	0.292 (5)
O6	0.187 (2)	0.232 (2)	0.171 (3)
N7	0.308 (3)	0.250 (2)	0.377 (5)
C8	0.433 (2)	0.320 (2)	0.333 (3)
C9	0.489 (2)	0.310 (2)	0.206 (3)
C10	0.614 (4)	0.368 (5)	0.173 (5)
C11	0.674 (4)	0.451 (6)	0.262 (5)
C12	0.617 (2)	0.463 (2)	0.394 (4)
C13	0.492 (2)	0.389 (2)	0.437 (0)

Table 1b. Thermal parameters with e.s.d.'s.

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C1	0.023 (3)	0.048 (2)	0.037 (3)	-0.028 (5)	-0.008 (2)	-0.048 (3)
C2	0.032 (7)	0.015 (7)	0.020 (5)	0.001 (4)	0.007 (2)	0.004 (8)
C3	0.040 (8)	0.011 (3)	0.140 (20)	-0.017 (7)	-0.043 (20)	-0.045 (13)
C4	0.012 (3)	0.011 (1)	0.015 (3)	-0.012 (3)	0.000 (6)	-0.007 (4)
C5	0.018 (3)	0.006 (3)	0.017 (3)	0.007 (2)	-0.003 (4)	-0.011 (4)
C6	0.025 (4)	0.022 (6)	0.006 (7)	-0.008 (8)	-0.010 (10)	0.008 (12)
N7	0.025 (1)	0.010 (1)	0.010 (3)	-0.009 (3)	-0.005 (2)	0.001 (1)
C8	0.014 (2)	0.013 (1)	0.014 (2)	-0.009 (2)	0.000 (3)	0.013 (3)
C9	0.021 (2)	0.011 (1)	0.012 (3)	-0.008 (2)	0.002 (1)	-0.004 (2)
C10	0.023 (3)	0.011 (5)	0.021 (2)	-0.009 (2)	-0.009 (1)	0.001 (4)
C11	0.014 (4)	0.016 (7)	0.026 (5)	-0.012 (1)	0.006 (1)	-0.002 (3)
C12	0.016 (2)	0.018 (2)	0.018 (3)	-0.001 (3)	-0.004 (2)	0.006 (3)
C13	0.014 (3)	0.011 (2)	0.021 (3)	-0.011 (4)	-0.002 (5)	-0.001 (4)

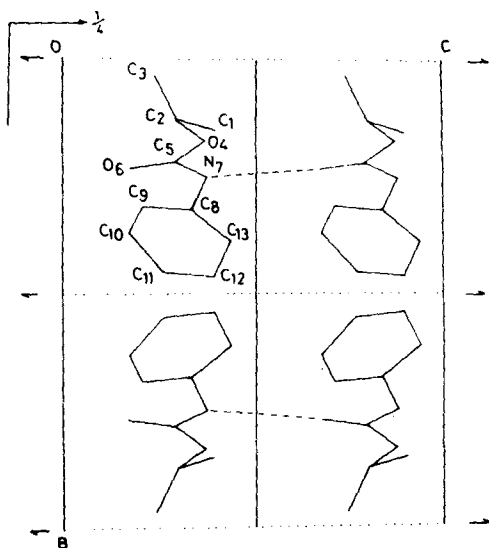
the temperature factor is of the form: $t = \exp - (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$.

planes is 31(4)°. This angle is 21° and 9° in the two independent molecules of isopropyl-*N* (methyl furoxan) (Calleri *et al* 1977).

It has been observed that in auxins, another class of plant hormones, where the carboxyl group is at the tail end of the molecule the angle between the rigid ring group and the carboxyl group is found to be 90° in active auxins and 0° in inactive auxins (Raghunathan and Vasantha Pattabhi 1981). *IPC* differs from auxins in having two methyl groups at the tail instead of a carboxyl group. The angle between the tail group viz. the plane through atoms C(1), C(2) and C(3) and the phenyl group is 32(4)°. However, the carbamate group makes 117(4)° with the plane through the tail group. In table 4, τ_2 refers to the angle between the rigid nucleus, like aromatic group and the plane through the three carbon atoms adjacent to the carbamate group (referred to as the tail group). From the table it can be inferred that though τ_1 varies from 0 to 180°, τ_2

Table 2. Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses.

C1—C2	1.59 (5)	C1—C2—C3	115 (3)
C2—C3	1.23 (5)	C1—C2—O4	101 (2)
C2—O4	1.43 (5)	C3—C2—O4	125 (3)
O4—C5	1.32 (6)	C2—O4—C5	113 (3)
C5—O6	1.19 (6)	O4—C5—O6	130 (3)
C5—N7	1.42 (6)	O4—C5—N7	107 (3)
N7—C8	1.46 (3)	O6—C5—N7	122 (3)
C8—C9	1.34 (4)	C5—N7—C8	125 (3)
C9—C10	1.36 (5)	N7—C8—C9	121 (2)
C10—C11	1.41 (8)	N7—C8—C13	114 (2)
C11—C12	1.40 (6)	C9—C8—C13	121 (2)
C12—C13	1.48 (3)	C8—C9—C10	119 (2)
C13—C8	1.40 (3)	C9—C10—C11	121(4)
		C10—C11—C12	120 (3)
		C11—C12—C13	119 (2)
		C12—C13—C8	115 (1)

**Figure 1.** Packing of the molecule down the *a* axis.**Table 3.** Distance of separation between the oppositely charged atoms in IPC. The average σ is about 0.04 Å.

N7 C1	4.47
N7 C3	4.27
C8 O4	3.61
C8 O6	2.91
C8 C1	5.82
C8 C3	5.53

Table 4. Conformational parameters in some carbamates

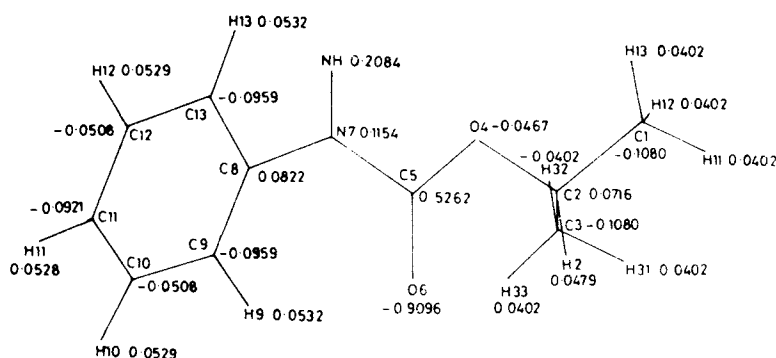
Name	NCOC(°)	CNCO(°)	τ_1 (°)	τ_2 (°)	References
Polyurethane	176.9 (7)	179.3 (6)	13.77	84.69	1
Ethyl carbamate	-179.24 (60)	0.96 (4)	1.50	—	2
DPBC	179.10 (36)	2.00 (68)	53.13	72.51	3
DPEC	179.81 (29)	—	—	59.9	3
INMF				70.3	
Isomer A	-179.53 (13)	92.50 (64)	159.13	88.77	4
Isomer B	171.15 (20)	3.93 (38)	54.70	50.30	4
IPC	-175 (3)	-170 (3)	31 (4) ^o	32.4	Present work

τ_1 Angle between the rigid nucleus like aromatic group and the carbamate group plane; τ_2 angle between the rigid nucleus and the tail group plane. 1. Foreier *et al* (1981); 2. Bracher *et al* (1967); 3. Cohen *et al* (1977); Calleri *et al* (1977).

has a preference for gauche conformation. The N-C-O-C (NCOC) group prefers *trans*-configuration in all the structures compared in table 4.

In order to compare the results obtained in this study with another class of plant hormones, viz., auxins, we have performed charge density calculations on the IPC molecule. The σ charges were calculated by the DelRe method (DelRe 1958) and the π charges using Huckel LCAO-MO method (Pullman and Pullman 1963). The net fractional charges on each atom is shown in figure 2. The distance of separation between the oppositely charged atoms of the ring group and the side chain are listed in table 3.

According to the charge separation theory on auxins (Porter and Thimann 1965) the critical distance of separation between the net positive charge present in the rigid nucleus and the carboxyl group oxygen is about 5.5 Å, for them to be active. An attempt has been made to see whether this theory can be applied to IPC, a different class of hormone, viz., carbamate. In IPC the distance of separation between the negatively charged methyl carbons and the positively charged C(8) atom of the ring are viz., C(8) . . . C(3) 5.53(5) and C(8) . . . C(1) 5.82(5) Å which can be compared.

**Figure 2.** Charge distribution in IPC.

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