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A Polarized Twisted Ethylene: (1,3-Dimethyl-2-imidazolidinylidene)phenylacetonitrile, $C_{13}H_{15}N_3$

By Nirupa Sen (née Kamath) and K. Venkatesan

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, *India*

and K. R. Acharya and T. N. Guru Row

National Chemical Laboratory, Poona 411 007, *India*

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Abstract. $M_r = 213\cdot13$, orthorhombic, $P2_12_12_1$, $a = 9\cdot858$ (2), $b = 10\cdot951$ (2), $c = 10\cdot984$ (2) Å, $V = 1185\cdot8$ Å^3, $Z = 4$, $D_m = 1\cdot191$ (2) (by flotation method in KI solution), $D_x = 1\cdot194$ (2) g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0\cdot41$ cm^{-1}, $F(000) = 456$, $T = 293$ K. Final $R = 0\cdot041$ for 875 significant reflections. The C=C bond length is 1·382 (4) Å, significantly longer than that in ethylene, 1·336 (2) Å. The molecule is twisted about the C=C bond by 23·1 (4)° and the phenyl group is rotated out of the plane of this bond by 39·4 (4)°. Molecular packing is determined by van der Waals forces.

Introduction. Polarized twisted ethylenes having donors such as the 1,3-dimethyl-2-imidazolidinylidene ring and phenyl and cyano groups as acceptors have been investigated by X-ray crystallography (Adhikesavalu, Kamath & Venkatesan, 1983; Abrahamsson, Rehnberg, Liljefors & Sandström, 1974; Sen & Venkatesan, 1984).

We have now investigated the molecular structure of (1,3-dimethyl-2-imidazolidinylidene)phenylacetonitrile with a strong donor and weak acceptor combination.

Experimental. Single crystals of title compound obtained from toluene by slow evaporation, approximate dimensions 0·2 × 0·4 × 0·6 mm. Preliminary Weissenberg photographs indicated that the crystals are orthorhombic. Lattice parameters refined using a least-squares fit to the settings for 25 accurately centered reflections. Nonius CAD-4-11M diffractometer, monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scan mode, $\theta \leq 24°$. During data collection three standard reflections (400, 004, 123) showed only statistical variation within ±2%. 1141 reflections collected, hkl range: h 0 to 11, k 0 to 12, l 0 to 12, 875 significant, $|F_o| \geq 3\sigma(|F_o|)$. Data not corrected for absorption. Structure solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix refinement (*SHELX*76; Sheldrick, 1976) of a scale factor, positional and anisotropic thermal parameters (isotropic thermal parameters for H atoms, located from a difference map) converged to $R = 0\cdot041$, $R_w = 0\cdot037$, $S = 1\cdot97$; $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 1\cdot2213/[\sigma^2(F) + 0\cdot00002|F_o|]$. Δ/σ for non-H atoms ~0·001. Final difference map featureless. Atomic scattering

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factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Positional coordinates of the non-H atoms are recorded in Table 1.* Table 2 gives some of the important torsion angles. Fig. 1 gives the view and the numbering scheme and Fig. 2 the bond lengths and angles for non-H atoms.

The C=C bond length of 1·382 (4) Å is signficantly longer than the C=C bond in ethylene [1·336 (2) Å; Bartell, Roth, Hollowell, Kuchitsu & Young, 1965]. The value in (1,3-dimethyl-2-imidazolidinylidene)-malononitrile is 1·407 (3) Å (Adhikesavalu & Venkatesan, 1982) and that in 3-(1,3-dimethyl-2-imidazolidinylidene)-2,4-pentanedione trihydrate is 1·468 (3) Å (Adhikesavalu & Venkatesan, 1983), indicating that the acceptor strength increases in the order Ph < CN < $COCH_3$.

The rotation about the C=C bond as measured by the angle between the planes through the atoms N(2), C(3), N(3) and C(8), C(2), C(1) is 23·1 (4)°. The phenyl group twists out of the plane of the ethylene bond by 39·4 (4)° whereas in 3-dimethylamino-3-methylthio-2-phenylacrylonitrile (Sen & Venkatesan, 1984) the phenyl group is rotated out of the plane of the group by 43·9 (4)°.

The conjugation has resulted in a shortening of the $\ddot{N}-C_{sp^2}$ (donor C) bonds [N(2)—C(3) 1·363 (4); N(3)—C(3) 1·360 (3) Å] in comparison with the corresponding N—C distances of 1·395 (3) and 1·403 (3) Å in *N,N',N'',N'''*-tetraphenyl-2,2'-bi-(imidazolidinylidene) (Hitchcock, 1979), while on the acceptor side the C(1)—C(2) bond of 1·418 (5) Å is shorter than the corresponding C—CN distance of 1·437 (2) Å in ethylenetetracarbonitrile (Little, Pautler & Coppens, 1971).

The imidazolidine ring is non-planar with approximate C_2 symmetry. The twofold axis passes through the atom C(3) and bisects the C(4)—C(5) bond. The torsion angles within this ring about the bonds C(4)—N(2), N(2)—C(3), C(3)—N(3), N(3)—C(5) and C(5)—C(4) are 12·9 (4), −5·6 (3), −4·7 (3), 12·4 (4) and −14·6 (4)°. The pyramidality at N(2) is −0·242 (3)° and at N(3) 0·252 (3)° with the N atoms deviating in opposite directions.

The value of χ[C(3)] is 3·1 (4)° and χ[C(2)] is 4·4 (4)° as calculated by the method described by Winkler & Dunitz (1971) for the out-of-plane bending of atoms.

Table 1. *Final positional (fractional) parameters for non-*H *atoms* ($\times 10^4$) *with equivalent isotropic temperature factors* ($\times 10^2$)

E.s.d.'s are given in parentheses. The temperature factor is of the form: $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}(Å^2)
N(1)	1055 (4)	1831 (3)	1978 (3)	8·82 (13)
C(1)	1159 (4)	1813 (3)	3018 (3)	6·13 (11)
C(2)	1271 (3)	1836 (3)	4305 (3)	4·87 (10)
C(3)	997 (3)	781 (2)	4949 (2)	4·67 (10)
N(2)	567 (3)	738 (2)	6127 (2)	5·30 (8)
N(3)	1052 (3)	−376 (2)	4500 (3)	6·15 (9)
C(4)	185 (5)	−506 (3)	6468 (4)	6·91 (14)
C(5)	747 (5)	−1266 (3)	5443 (4)	7·28 (14)
C(6)	−160 (5)	1711 (4)	6731 (4)	6·49 (13)
C(7)	2003 (6)	−745 (5)	3569 (6)	9·48 (21)
C(8)	1591 (3)	3038 (2)	4840 (3)	4·59 (9)
C(9)	2487 (3)	3144 (3)	5818 (3)	5·32 (11)
C(10)	2828 (4)	4264 (3)	6290 (3)	6·24 (12)
C(11)	2297 (4)	5313 (3)	5787 (4)	6·73 (13)
C(12)	1427 (4)	5230 (3)	4822 (4)	6·95 (13)
C(13)	1069 (4)	4115 (3)	4361 (3)	6·06 (12)

Table 2. *Some important torsion angles* (°)

N(2)—C(3)—C(2)—C(1)	−154·1 (3)	N(3)—C(3)—C(2)—C(8)	−161·6 (3)
N(2)—C(3)—C(2)—C(8)	21·5 (5)	C(3)—C(2)—C(8)—C(9)	43·8 (5)
N(3)—C(3)—C(2)—C(1)	22·7 (4)	C(3)—C(2)—C(8)—C(13)	−139·3 (3)

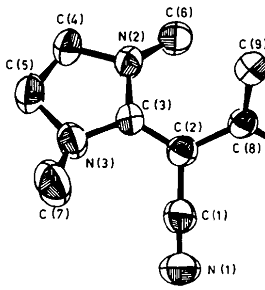

Fig. 1. A perspective view of the molecule viewed down the *a* axis with the numbering scheme.

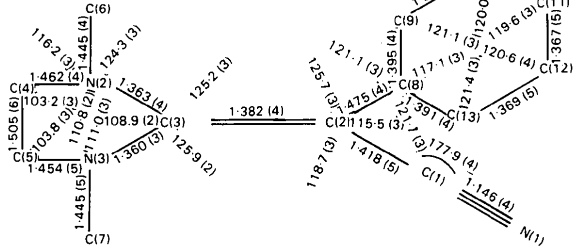

Fig. 2. Bond lengths (Å) and angles (°) of non-H atoms (e.s.d.'s are given in parentheses).

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* Lists of structure factors, anisotropic thermal parameters, H-atom positions and their isotropic temperature factors and bond lengths and angles for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39702 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

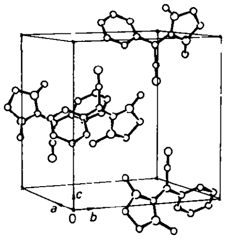

Fig. 3. Packing of the molecules viewed down the *a* axis.

The NMR rotational barrier is 39·7 kJ mol^{-1} (Sandström, Sjostrand & Wennerbeck, 1977) for the title compound and 59·4 kJ mol^{-1} (Sandström, 1983) for 3-dimethylamino-3-methylthio-2-phenylacrylonitrile. We have earlier observed a correlation between rotational barrier *vs* C=C bond length in push–pull systems (Kamath & Venkatesan, 1984). However, surprisingly the above-mentioned two compounds having the same weak acceptor combination of (—Ph, —CN) deviate from the observed correlation referred to above. The reason for this deviation is not obvious.

There are no intermolecular contacts of any special significance and the molecule is mostly stabilized by van der Waals interactions (Fig. 3). The illustrations were made with the *ORTEP*II program (Johnson, 1976).

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α-Méthyl-dopa, $C_{10}H_{13}NO_4.1,5H_2O$

PAR A. NEUMAN, H. GILLIER ET D. AVENEL

Laboratoire de Chimie Structurale Biomoléculaire, UER Santé, Médecine et Biologie Humaine, Université Paris-Nord, 74 rue Marcel Cachin, 93012 Bobigny CEDEX, France

ET G. PERRET

Laboratoire de Pharmacologie Clinique et Expérimentale, UER Santé, Médecine et Biologie Humaine, Université Paris-Nord, 74 rue Marcel Cachin, 93012 Bobigny CEDEX, France

(*Reçu le* 20 *mars* 1984, *accepté le* 6 *septembre* 1984)

Abstract. $M_r = 238$, monoclinic, $P2_1$, $a = 14{\cdot}30\ (1)$, $b = 8{\cdot}678\ (5)$, $c = 8{\cdot}911\ (5)$ Å, $\beta = 96{\cdot}57\ (1)°$, $V = 1098{\cdot}55$ Å^3, $Z = 4$, $D_x = 1{\cdot}439$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 10{\cdot}12$ cm^{-1}, $F(000) = 508$, $T = 298$ K, $R = 0{\cdot}049$ for 3402 reflexions. The two symmetrically independent molecules show the two *gauche* conformations of the nitrogen atom relative to the C(7)—C(8) bond with the carboxylic group *gauche* in