the same time its stereospecificity is indicated by the *anti* orientation of the pyridine ring with respect to the cyano group (Fruttero *et al.*, 1984) the mutual orientation corresponding to that of calvatic acid (Viterbo *et al.*, 1975). The individual bond distances of the azoxycyano group are identical, within the standard deviations, in (1) and (2) excepting bond N(2)—O which is 1·244 (2) Å here and 1·218 (7) Å in (1). Also here its length remains shorter than in other azoxycyano compounds (range 1·26–1·30 Å; Hoesch & Weber, 1977; Cotrait, Marsau & Pasquer, 1979, and references therein; Lamotte, Dupont, Dideberg, Dive & Jamoulle, 1980). The $-\mathrm{N(O^-)=N-C\equiv N}$ moiety in (2) is not strictly planar: only the $-\mathrm{N=N-C\equiv N}$ group does not deviate significantly from planarity, with O(2) at 0·021 (2) Å out of the mean plane; instead, in calvatic acid (1) the whole azoxycyano group is planar (Viterbo *et al.*, 1975).

The pyridine ring is planar. The C—C distances are tightly distributed around their mean, 1·378 (2) Å, which is smaller than the value obtained for pyridine both by X-ray analysis, 1·392 (1) Å (Sörensen, Mahler & Rastrup-Andersen, 1974), and by microwave measurements, 1·3945 (2) Å (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958). A similar trend was found in 3,5-dinitropyridine (Destro, Pilati & Simonetta, 1974), in picolinamide (Takano, Sasada & Kakudo, 1966) and in 2,5-pyridinedicarboxylic acid (Ito, Kashino & Haisa, 1976). The electron-withdrawing substituent at C(2), Fig. 1, also shortens bond N(1)—C(2) with respect to N(1)—C(6), Table 2, and induces a widening of the N(1)—C(2)—C(3) angle (Domenicano, Vaciago & Coulson, 1975). The dihedral angle between the planes through the pyridine and the azoxycyano groups is 5·8 (1)°, larger than in (1) [2·8 (1)°]. The preference, shown in the solid state, for the conformation with C(3)—H(3) on the same side of O, Fig. 1, is probably due to destabilization of the other conformer owing to repulsion between the lone pair of N(1) and the negatively charged O atom.

The packing of the molecules in the crystal reveals no intermolecular contacts shorter than the sums of the van der Waals radii.

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Acta Cryst. (1984). C**40**, 1730–1733

Polarized Twisted Ethylenes: Structure of 3-Dimethylamino-3-methylthio-2-phenylacrylonitrile, $C_{12}H_{14}N_2S$

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(*Received* 16 *March* 1984; *accepted* 30 *May* 1984)

Abstract. $M_r = 218$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 8{\cdot}140$ (2), $b = 10{\cdot}434$ (2), $c = 14{\cdot}101$ (3) Å, $V = 1197{\cdot}6$ Å^3, $D_m = 1{\cdot}204$ (3) (by flotation method in KI solution), $D_x = 1{\cdot}209$ (3) g cm^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å) $= 2{\cdot}29$ cm^{-1}, $F(000) = 464$, $T = 293$ K, $R = 3{\cdot}9\%$, 1169 significant reflections. The $\mathrm{C-N(CH_3)_2}$

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bond distance is 1·355 (4) Å, and the C=C bond length is 1·369 (5) Å. The molecule is twisted about the C=C bond by 22·2 (3)°. The packing of the molecules is controlled by van der Waals interactions.

Introduction. The title compound, which belongs to the class of ketene *N,S*-aminals, was studied as part of a research programme on the X-ray crystallographic studies of push–pull ethylenes with different donors and acceptors (Adhikesavalu, Kamath & Venkatesan, 1983). The results obtained for the title compound are presented here.

Experimental. Single crystals from methanol by slow evaporation. Crystal approx. 0·2 × 0·4 × 0·5 mm. Preliminary Weissenberg photographs indicated that the crystals are orthorhombic. Nonius CAD-4 diffractometer used for refining lattice parameters using a least-squares fit to the settings for 22 accurately centred reflections. Intensity data collected using monochromated Mo $K\alpha$ radiation. $\omega/2\theta$ scan mode, scan speed 1° min^{-1}. $2\theta_{\max} = 47{\cdot}0°$. h 0 to 10, k 0 to 12, l 0 to 17. Two standard reflections (221 and 112) showed only statistical variations within ±2%. Total of 1462 reflections collected, 1169 significant [$|F_o| \geq 3\sigma(|F_o|)$]. Data not corrected for absorption. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix refinement of a scale factor, positional and anisotropic thermal parameters (isotropic thermal parameters for H atoms, located from a difference map) converged to $R = 0{\cdot}039$, $R_w = 0{\cdot}044$, $S = 1{\cdot}65$; $w = 1{\cdot}3563/[\sigma^2(F) + 0{\cdot}00200|F_o|^2]$. *SHELX*76 (Sheldrick, 1976) used for full-matrix refinement. For non-hydrogen atoms $\Delta/\sigma \approx 0{\cdot}008$. Final difference map featureless. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

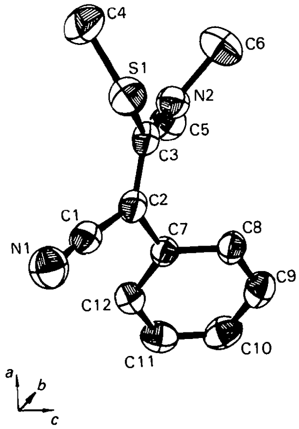

Fig. 1. A perspective view of the molecule viewed down **b**, with the numbering scheme.

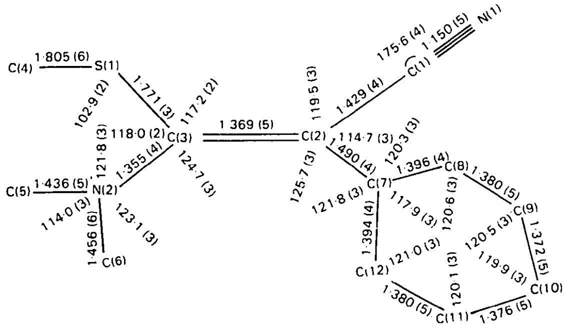

Fig. 2. Bond lengths (Å) and angles (°) of the non-hydrogen atoms (e.s.d.'s in parentheses).

Table 1. *Final (fractional) coordinates* (×10^4) *and equivalent isotropic temperature factors of the non-hydrogen atoms* (×10^2) (*e.s.d.'s in parentheses*)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$(Å^2)
S(1)	10091 (1)	1180 (1)	5636 (1)	5·65 (0·03)
C(1)	6955 (4)	−72 (3)	5142 (2)	4·68 (0·09)
C(2)	7803 (4)	−637 (3)	5925 (2)	4·01 (0·08)
C(3)	9401 (4)	−303 (3)	6100 (2)	4·24 (0·08)
C(7)	6794 (3)	−1531 (3)	6508 (2)	3·70 (0·08)
C(8)	6823 (4)	−1452 (3)	7497 (2)	4·27 (0·08)
C(9)	5868 (5)	−2262 (3)	8040 (2)	5·12 (0·10)
C(10)	4885 (5)	−3165 (4)	7619 (3)	5·69 (0·10)
C(11)	4838 (5)	−3261 (4)	6646 (3)	5·69 (0·11)
C(12)	5768 (4)	−2443 (3)	6095 (2)	4·90 (0·10)
C(4)	12029 (7)	763 (7)	5095 (4)	8·25 (0·19)
C(5)	10275 (5)	−2362 (4)	6745 (3)	5·72 (0·12)
C(6)	11678 (6)	−431 (5)	7256 (4)	6·95 (0·16)
N(2)	10468 (3)	−1004 (3)	6624 (2)	4·88 (0·08)
N(1)	6184 (4)	342 (4)	4531 (2)	6·98 (0·12)

Discussion. A perspective view and the numbering scheme with bond lengths and angles for non-hydrogen atoms for the title compound (I) are shown in Figs. 1 and 2 respectively. Positional coordinates of non-hydrogen atoms are in Table 1.* Table 2 gives some of the important torsion angles.

In the ketene *N,S*-aminals studied earlier in our laboratory, 2-benzoyl-3-dimethylthioacrylonitrile (II) (Adhikesavalu & Venkatesan, 1981) and [dimethylamino(methylthio)methylene]malononitrile (III) (Adhikesavalu & Venkatesan, 1983), the C=C double-bond lengths are 1·414 (4) and 1·397 (8) Å respectively and the twists about the C=C bonds are 38·3 and 21·7° respectively. In the title compound the C=C bond length is 1·369 (5) Å and the twist is

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39548 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

C(1)–C(2)–C(3)–S(1)	21·9 (4)	C(3)–C(2)–C(7)–C(8)	43·9 (4)	C(7)–C(2)–C(3)–N(2)	22·1 (5)
C(1)–C(2)–C(3)–N(2)	−160·2 (3)	C(3)–C(2)–C(7)–C(12)	−137·8 (3)	C(7)–C(8)–C(9)–C(10)	0·5 (5)
C(1) C(2) C(7)–C(8)	−133·9 (3)	C(4)–S(1)–C(3)–C(2)	−132·9 (9)	C(8)–C(7)–C(12)–C(11)	−1·4 (17)
C(2)–C(3)–N(2)–C(6)	−142·5 (4)	C(4)–S(1)–C(3)–N(2)	49·0 (3)	C(8)–C(9)–C(10)–C(11)	−0·5 (6)
C(2)–C(7)–C(8)–C(9)	178·8 (3)	S(1)–C(3)–N(2)–C(5)	−157·5 (3)	C(9)–C(10)–C(11)–C(12)	−0·5 (10)
C(2)–C(3)–N(2)–C(5)	24·7 (5)	S(1)–C(3)–N(2)–C(6)	35·4 (4)	C(10)–C(11)–C(12)–C(7)	1·5 (18)
C(2)–C(7)–C(12)–C(11)	−179·8 (9)	C(7)–C(2)–C(3)–S(1)	−155·8 (2)	C(12)–C(7)–C(8)–C(9)	0·4 (9)

22·2 (3)°. The bond length is significantly longer than the value for this bond in ethylene [1·336 (2) Å (Bartell, Roth, Hollowell, Kuchitsu & Young, 1965)]. The donor groups remaining the same in the above examples, the significantly shorter C=C bond length in the title compound indicates that the phenyl group is a poorer acceptor than the cyanide group. Further, the phenyl group twisting out of the plane of the ethylene bond [43·9 (4)°] would be expected to interact with the C=C bond less effectively. In (III), the $\Delta G\ddagger$ of the C=C bond is 55·2 kJ mol^{-1} and the $\Delta G\ddagger$ of the C_{donor}–N bond is 46·4 kJ mol^{-1}. In the title compound (I), $\Delta G\ddagger$ of the C_{donor}–N bond is 37 kJ mol^{-1} (Sandström, 1983). The lowering of the barrier of the C–N bond in (I) as compared to (III) also increases its freedom to rotate out-of-plane from the double bond, resulting in a shortening of the C=C bond.

The '*Z*' form as defined by Sandström (1983), in which the –NMe$_2$ and –Ph groups are *cis* to each other, predominates in solution as the major conformer. Our X-ray investigations indicate that even in the solid state the '*Z*' form persists. This is surprising since the '*Z*' form from steric considerations alone is more congested than the '*E*' form. One possible reason for '*Z*' being the major conformer could be the efficient conjugation when the strongest donor (NMe$_2$) and the strongest acceptor (–CN) are *trans* related. Further, as observed by Sandström & Wennerbeck (1978), the preference for the '*Z*' form may be due to its better solvation in polar solvents owing to the higher dipole moment of the '*Z*' form. We obtained the crystals from a polar solvent, methanol.

We have earlier observed a correlation between the rotational barrier *vs* C=C bond length in the push–pull systems (Kamath & Venkatesan, 1984). However, the C=C value of 1·369 (5) Å for the title molecule and the rotational barrier of 59·4 kJ mol^{-1} measured by the DNMR technique (Sandström, 1983) deviate from the observed correlation referred to above. For the C=C value of 1·369 (5) Å, the rotational barrier would be expected to be larger (*i.e.* about 80 kJ mol^{-1}) whereas the measured value in dichlorofluoromethane is 59·4 kJ mol^{-1} (Sandström, 1983).

It is difficult to attribute the deviation of the present structure from the correlation between $\Delta G\ddagger$ *vs* l(C=C) to any single reason. As mentioned earlier, the phenyl group is rotated out of the plane of the group by 43·9°. This would reduce the conjugation involving the C=C bond which results in a shorter C=C bond length. More importantly, one does not have any idea of the transition-state geometry of the molecule which becomes relevant for the consideration of the rotation-barrier energy.

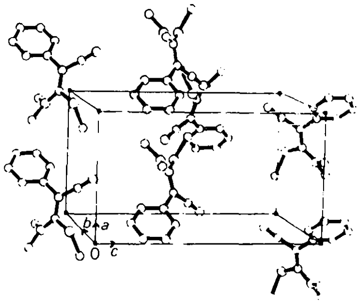

Fig. 3. Packing of the molecules viewed down **b**.

The N(2)–C(3) distance in (I) [1·355 (4) Å] is shorter than in (II) [1·318 (5) Å] and (III) [1·333 (7) Å] which is consistent with less delocalization involving the C=C bond in the present molecule.

The out-of-plane bending at atoms C(1) and C(2) was calculated using the method described by Winkler & Dunitz (1971). The value of χ[C(2)] is 2·3 (3)° and χ[C(3)] is 2·1 (4)°. Also, N(2) deviates from the plane of the bonded atoms by 0·087 (3) Å. The torsion angle C(2)–C(3)–N(2)–C(5) is 24·7 (5)°. The orientation of the methyl group on S is away from the cyano group, the torsion angle C(2)–C(3)–S(1)–C(4) being −132·9 (9)°.

The packing of the molecules is dictated mainly by van der Waals interactions and is displayed in Fig. 3. The illustrations were made with the *ORTEP*II program (Johnson, 1976).

We thank the University Grants Commission of India for financial support. We are grateful to Professor J. Sandström, University of Lund, Sweden, for many valuable comments.

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Acta Cryst. (1984). C**40**, 1733–1734

Structure of Urea–Oxalic Acid (1/1), $CH_4N_2O.C_2H_2O_4$, Determined by Neutron Diffraction*

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(*Received* 12 *December* 1983; *accepted* 12 *June* 1984)

Abstract. $M_r = 150{\cdot}1$, monoclinic, $C2/c$, $a = 13{\cdot}0625\,(7)$, $b = 6{\cdot}6437\,(2)$, $c = 6{\cdot}8478\,(3)$ Å, $\beta = 92{\cdot}474\,(6)°$, $U = 593{\cdot}72$ Å^3, $Z = 4$, $D_x = 1{\cdot}68$ g cm^{-3}, $\lambda = 1{\cdot}275$ Å, $\mu = 1{\cdot}49$ cm^{-1}, $T = 295\,(1)$ K. Final $R = 6{\cdot}2\%$ for 757 independent observed reflexions. The crystal structure contains urea and oxalic acid molecules, held together by a two-dimensional hydrogen-bonding network. The neutron diffraction experiment provides a more accurate description of the geometry of the hydrogen bonds than the corresponding X-ray experiment [Harkema & ter Brake (1979). *Acta Cryst.* B**35**, 1011–1013].

Introduction. Urea and oxalic acid can form two different addition compounds with ratio 1:1 or 2:1. The crystal structure of these compounds has been determined by X-ray diffraction (Harkema & ter Brake, 1979; Harkema, Bats, Weijenberg & Feil, 1973). Both compounds have been studied in our laboratory in order to obtain accurate electron densities. To obtain more accurate hydrogen parameters a neutron diffraction experiment was carried out, the results of which are presented here.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^4$)

	x	y	z	U_{eq}*
C(1)	0	7861 (3)	2500	276 (5)
C(2)	2135 (1)	1654 (2)	4651 (2)	257 (4)
N(1)	762 (1)	6853 (2)	3414 (2)	395 (4)
O(1)	0	9752 (3)	2500	347 (7)
O(2)	1330 (1)	2345 (3)	3678 (3)	334 (5)
O(3)	2309 (1)	−86 (3)	5001 (3)	395 (5)
H(1)	1328 (3)	7634 (6)	4095 (6)	499 (11)
H(2)	836 (3)	5356 (5)	3362 (7)	558 (13)
H(3)	856 (2)	1193 (5)	3246 (5)	422 (9)

* Defined according to Willis & Pryor (1975).

Experimental. A crystal suitable for neutron diffraction work (1·9 × 4·1 × 4·2 mm) was prepared by slow evaporation of a solution of 8 g urea and 84 g oxalic acid dihydrate in 220 ml of water at 313 K (Dalman, 1934); neutron data collected on a four-circle diffractometer at the HFR reactor at Petten, wavelength of 1·275 Å obtained after diffraction from the (311) planes of the copper crystals of a double monochromator; ω–2θ step scans (0·0625° step^{-1}); results processed by the procedure of Lehmann & Larsen (1974); reflexions with $\theta < 65°$ (approx. 3750), equivalents averaged, $R_{int} = 4{\cdot}5\%$, insignificant reflexions $[I < \sigma(I)]$ omitted, 757 independent reflexions; index range $h \pm 18$, $k\,0$–9, $l\,0$–9; reference reflexion

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* Supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

0108-2701/84/101733-02$01.50