

Tabelle 3. Liste der Struktur Faktoren zur Bestimmung der absoluten Konfiguration

Index	$[F_o(hkl)/F_o(\bar{h}\bar{k}\bar{l})] - 1$	$[F_c(hkl)/F_c(\bar{h}\bar{k}\bar{l})] - 1$	Index	$[F_o(hkl)/F_o(\bar{h}\bar{k}\bar{l})] - 1$	$[F_c(hkl)/F_c(\bar{h}\bar{k}\bar{l})] - 1$
5 -1 2	-0.180	-0.243	-2 2 0	-0.122	-0.106
4 1 1	-0.105	-0.092	-2 -1 2	0.307	0.274
2 1 4	-0.106	-0.112	-2 -1 1	0.142	0.130
2 -1 2	0.204	0.194	-2 -2 1	-0.087	-0.082
1 1 1	-0.094	-0.122	-2 -3 1	0.220	0.194
1 -1 1	0.220	0.244	-3 0 1	0.066	0.061
1 -2 2	0.068	0.064	-3 1 1	-0.103	-0.101
0 2 0	-0.071	-0.089	-3 -1 1	-0.041	-0.038
0 1 3	-0.115	-0.120	-4 1 1	0.104	0.108
0 -1 7	0.084	0.160	-4 -1 5	-0.114	-0.115
0 -4 3	-0.090	-0.090	-4 -1 1	-0.088	-0.091
-1 -2 1	-0.043	-0.034	-6 0 2	-0.069	-0.056
-1 -3 1	0.055	0.100	-6 -1 3	0.192	0.198
-1 -4 1	-0.105	-0.092	-6 -1 2	0.167	0.207
-1 -5 2	0.104	0.110	-7 1 2	-0.373	-0.321

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## Polarized Ethylenes: Structure of 2-Benzoyl-3-dimethylamino-3-methylthio-2-propenenitrile

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## Abstract

$C_{13}H_{14}N_2OS$ ,  $M_r = 246$ , is monoclinic,  $P2_1/c$ , with  $a = 7.214$  (1),  $b = 8.935$  (5),  $c = 20.243$  (6) Å,  $\beta = 99.42$  (2)°,  $V = 1304.83$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.23$ ,  $D_x = 1.25$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha, \lambda = 0.7107 \text{ Å}) = 0.232$  mm<sup>-1</sup>,  $F(000) = 520$ . The structure was solved by direct methods and refined to an  $R$  value of 0.042 using 1127 intensity measurements. The C=C and C-N bond distances differ considerably from their normal values. An appreciable rotation [38.3(4)°] about the C=C bond is observed, the bond length being 1.414(5) Å. This is due to the combination of push-pull and steric effects.

## Introduction

Ethylenes substituted with electron-donating and electron-withdrawing groups in the vicinal positions exhibit interesting behaviour. For example, the strong conjugative interaction between the donor and acceptor part of the molecule leads to chemically stabilized double bonds, so that they are resistant to oxidation and reduction and to addition of bromine under normal conditions (Jensen & Henriksen, 1968). Furthermore, the conjugative interaction results in lengthening of the C=C bond and shortening of donor-ethylenic-carbon and acceptor-ethylenic-carbon bond distances. Simultaneously the barrier to rotation about the C=C bond is

drastically reduced (Shvo, Taylor & Bartulin, 1967). Whereas in 1,2-dideuterioethylene it is 261.2 kJ mol<sup>-1</sup> (Douglas, Rabinovitch & Looney, 1955; Rabinovitch & Michael, 1959), in some of the polarized ethylenes it is less than 42 kJ mol<sup>-1</sup> (Shmueli, Shanan-Atidi Horwitz & Shvo, 1973; Wennerbeck & Sandström, 1973). The potential-energy curve for the rotation about the double bond in an olefin is the sum of two potential curves, one due to the  $\pi$ -electron energy and the other due to the steric strain (Sandström & Sjöstrand, 1978). The loss of  $\pi$ -electron conjugation energy reaches its maximum at the dihedral angle  $\theta = 90^\circ$ , where the lack of overlap between the two ethylenic orbitals destabilizes the system, whereas the steric strain due to non-bonded repulsion between substituents on the two ethylenic C atoms is at its maximum at  $\theta = 0^\circ$ .

Although X-ray analysis results on a few polarized ethylenes and related compounds have been reported (Shmueli *et al.*, 1973; Abrahamsson, Rehnberg, Liljefors & Sandström, 1974; Shimanouchi, Ashida, Sasada & Kakudo, 1967; Ammon & Plastas, 1971; Hazell & Mukhopadhyay, 1980), no systematic investigation of this interesting class of molecules has been carried out so far. We have undertaken such a study in our laboratory. It is hoped that this will lead to a correlation between barrier to rotation about the C=C bond, as determined from NMR investigations, and the C=C bond lengths from X-ray measurements. Furthermore, it would be of interest to study in favourable cases, the nature of the variations of electron densities in the C=C bond using accurate intensity measurements. We report in this paper our findings on the molecular geometry of 2-benzoyl-3-dimethylamino-3-methylthio-2-propenenitrile. The compound was kindly provided by Professor Jan Sandström, University of Lund, Sweden.

### Experimental

Single crystals of the compound were obtained from a toluene–ligroin mixture by slow evaporation. The crystal used in the data collection had the approximate dimensions 0.4 × 0.2 × 0.2 mm. Preliminary Weissenberg photographs indicated that the crystals are monoclinic, space group  $P2_1/c$ . Intensity data were collected on an Enraf–Nonius CAD-4 diffractometer using monochromated Mo  $K\alpha$  radiation by the  $\omega/2\theta$  mode to a limit of  $\theta = 23^\circ$  using a scan speed of 1° min<sup>-1</sup>. Two reflections were checked after every 100 reflections and they showed only statistical fluctuations. 1600 reflections were collected of which 1127 were significant,  $|F_o| \geq 2\sigma(|F_o|)$ . Corrections were not made for absorption.

### Structure solution and refinement

The structure was solved using the direct methods program *SHELX 76* (Sheldrick, 1976) in the space group  $P2_1/c$ . Block-diagonal least-squares refinement of a scale factor, atomic coordinates and anisotropic thermal parameters for the non-H atoms, using the program originally due to Shiono (1968) and modified by B. S. Reddy to suit an IBM 360/44 computer, gave an  $R$  index of 0.08. The H atoms were located from a difference synthesis. Full-matrix refinement of positional and anisotropic thermal parameters for non-H atoms and positional and isotropic temperature factors for H atoms gave a final  $R$  index of 0.042. The function minimized was  $\sum w(|F_o| - |F_c|)^2$  and the unit weighting scheme was found to be satisfactory.

### Discussion

Positional coordinates of non-H atoms and H atoms are given in Tables 1 and 2.\* Bond lengths and bond angles involving non-H atoms are given in Tables 3 and 4. Table 5 gives some of the important torsion angles and Fig. 1 gives the perspective view of the molecule.

\* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36059 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\times 10^2$ ) for non-H atoms with *e.s.d.*'s in parentheses

$$B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq}$ (Å <sup>2</sup> )
S	12782 (2)	1275 (1)	4957 (1)	523 (3)
O	9658 (3)	2668 (3)	3017 (1)	482 (9)
N(1)	11139 (5)	125 (3)	3831 (2)	453 (10)
N(2)	8331 (5)	3269 (4)	5204 (2)	628 (13)
C(1)	13049 (6)	3203 (5)	5191 (2)	589 (14)
C(2)	12908 (7)	-661 (5)	3781 (2)	593 (14)
C(3)	9497 (7)	-449 (5)	3378 (2)	566 (14)
C(4)	11009 (5)	1230 (4)	4252 (2)	370 (10)
C(5)	9521 (5)	2279 (4)	4157 (2)	355 (10)
C(6)	8852 (5)	2846 (4)	4731 (2)	427 (12)
C(7)	8884 (5)	2928 (4)	3505 (2)	370 (10)
C(8)	7236 (5)	3974 (4)	3410 (2)	369 (11)
C(9)	7348 (6)	5272 (5)	3050 (2)	503 (13)
C(10)	5819 (9)	6188 (6)	2895 (2)	686 (17)
C(11)	4143 (9)	5809 (7)	3073 (3)	767 (21)
C(12)	3980 (6)	4520 (7)	3431 (3)	671 (17)
C(13)	5549 (6)	3595 (5)	3614 (2)	488 (10)

Table 2. Fractional coordinates ( $\times 10^3$ ) and isotropic temperature factors for H atoms with e.s.d.'s in parentheses

The temperature factor is of the form  $T = \exp(-B \sin^2 \theta/\lambda^2)$ .

Bonded to		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
H(1)	C(1)	1254 (5)	387 (5)	485 (2)	4.3 (1.0)
H(2)	C(1)	1209 (5)	339 (4)	544 (2)	4.0 (1.0)
H(3)	C(1)	1435 (7)	341 (6)	533 (2)	7.4 (1.4)
H(4)	C(2)	1409 (6)	-1 (5)	396 (2)	6.4 (1.3)
H(5)	C(2)	1289 (5)	-157 (4)	401 (2)	3.6 (1.0)
H(6)	C(2)	1293 (5)	-90 (5)	335 (2)	4.0 (1.0)
H(7)	C(3)	830 (5)	-11 (4)	359 (2)	3.1 (1.0)
H(8)	C(3)	963 (7)	-10 (6)	290 (2)	6.6 (1.4)
H(9)	C(3)	941 (5)	-156 (5)	336 (2)	4.0 (1.0)
H(10)	C(9)	863 (5)	554 (4)	291 (2)	2.5 (0.8)
H(11)	C(10)	599 (6)	725 (5)	270 (2)	6.3 (1.3)
H(12)	C(11)	295 (7)	624 (6)	300 (3)	7.8 (1.5)
H(13)	C(12)	283 (5)	422 (5)	362 (2)	4.1 (1.0)
H(14)	C(13)	552 (4)	260 (4)	383 (2)	2.3 (0.8)

Table 3. Bond lengths (Å) with e.s.d.'s in parentheses

S—C(1)	1.789 (5)	C(7)—O	1.233 (4)
S—C(4)	1.755 (4)	C(7)—C(8)	1.500 (5)
N(1)—C(2)	1.474 (6)	C(8)—C(9)	1.380 (6)
N(1)—C(3)	1.467 (6)	C(9)—C(10)	1.368 (8)
N(1)—C(4)	1.318 (5)	C(10)—C(11)	1.360 (9)
C(4)—C(5)	1.414 (5)	C(11)—C(12)	1.377 (9)
C(5)—C(6)	1.423 (5)	C(12)—C(13)	1.402 (7)
C(6)—N(2)	1.148 (6)	C(13)—C(8)	1.390 (6)
C(5)—C(7)	1.446 (5)		

Table 4. Bond angles (°) with e.s.d.'s in parentheses

C(1)—S—C(4)	105.6 (2)	C(5)—C(7)—O	122.5 (3)
C(2)—N(1)—C(4)	123.7 (3)	C(6)—C(5)—C(7)	120.3 (3)
C(2)—N(1)—C(3)	114.3 (3)	C(5)—C(7)—C(8)	119.6 (3)
C(3)—N(1)—C(4)	122.0 (3)	C(7)—C(8)—C(9)	118.6 (3)
S—C(4)—N(1)	115.0 (3)	C(7)—C(8)—C(13)	121.6 (3)
S—C(4)—C(5)	122.1 (3)	C(8)—C(9)—C(10)	120.6 (4)
N(1)—C(4)—C(5)	122.8 (3)	C(9)—C(10)—C(11)	120.6 (5)
C(4)—C(5)—C(6)	118.4 (3)	C(10)—C(11)—C(12)	120.3 (6)
C(4)—C(5)—C(7)	120.7 (3)	C(11)—C(12)—C(13)	119.9 (5)
C(5)—C(6)—N(2)	178.2 (4)	C(12)—C(13)—C(8)	119.1 (4)

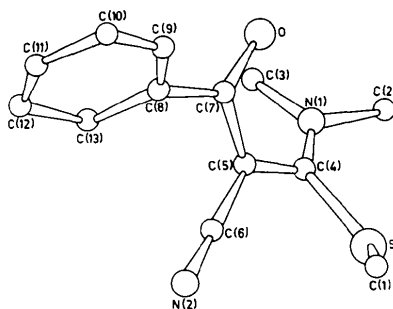


Fig. 1. Perspective view of the molecule.

Table 5. Torsion angles (°) with e.s.d.'s in parentheses

S—C(4)—C(5)—C(6)	-32.7 (5)	C(2)—N(1)—C(4)—C(5)	158.8 (4)
N(1)—C(4)—C(5)—C(6)	145.2 (4)	C(1)—S—C(4)—C(5)	-30.9 (4)
S—C(4)—C(5)—C(7)	138.2 (3)	C(5)—C(7)—C(8)—C(13)	-51.1 (5)
N(1)—C(4)—C(5)—C(7)	-43.9 (5)	C(5)—C(7)—C(8)—C(9)	135.6 (4)
C(4)—C(5)—C(7)—C(8)	176.7 (3)		

The C=C bond distance in unsubstituted ethylene is 1.314 (6) Å (van Nes & Vos, 1977). The C=C bond distance in this compound is 1.414 (5) Å, which is significantly longer than the reported value. The rotation about the C=C bond as measured by the angle between the plane through S, N(1) and C(4) and that formed by C(5), C(6) and C(7) is 38.3 (4)°. This C=C bond lengthening and the rotation about this bond must be attributed to the combined effect of conjugation and steric factors. The N(1)—C(4) bond length is 1.318 (5) Å, which is significantly shorter than the normal value of 1.426 (12) Å (*International Tables for X-ray Crystallography*, 1968) for a C(sp<sup>2</sup>)-N single bond, showing a partial double-bond character for this bond. On the acceptor side, the C(5)—C(7) bond length is 1.446 (5) Å which is shorter than 1.462 (9) Å (Lynch, Mellor & Nyburg, 1971), the value reported for a C(sp<sup>2</sup>)-C(sp<sup>2</sup>) single bond in a similar system. Conjugation results in lengthening of the C(7)=O bond as expected. The normal value for a C=O bond is 1.206 (6) Å (Usha, 1980; Cameron & Cordes, 1979; Lynch *et al.*, 1971) and the value found is 1.233 (4) Å. The C(5)—C(6) bond distance is 1.423 (5) Å whereas the value expected is 1.426 (5) Å (Sutton, 1965). The cyanide bond length is 1.148 (6) Å which is in agreement with the standard value of 1.157 (5) Å. Similarly there are no significant changes in the bonds involving the S atom. The S—C(4) bond distance is 1.755 (4) Å whereas the value reported for a S—C(sp<sup>2</sup>) bond is 1.766 (6) Å (Lynch *et al.*, 1971). As the methylthio group is a poor donor compared with the dimethylamino group, its participation in the conjugation is not expected to be significant.

The steric pressure arising from the intramolecular short contact between the O atom and the C(3) atom is relieved by the rotation about the C=C bond. However, rotation about the C(4)—C(5) bond results in a loss of conjugation. Intramolecular overcrowding could be overcome by rotation about the C(5)—C(7) bond. Such a situation is observed in dimethyl (dimethylaminomethylene)malonate (Shmueli *et al.*, 1973) where the methoxycarbonyl group *cis* to the dimethylamino group is pushed out of the plane of the molecule. The rest of the molecule is planar, with the dimethylamino group and the *trans* methoxycarbonyl group being in conjugation. In the present case such a situation would completely prohibit the benzoyl group's participation in conjugation. The push-pull effect reduces the energy barrier for rotation by reducing the  $\pi$ -overlap between the C(4) and C(5) atoms, and this facilitates the

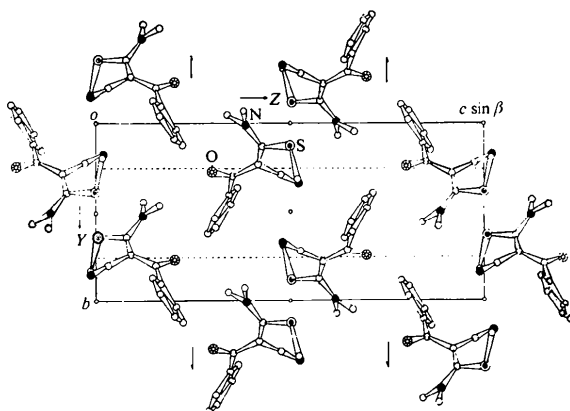


Fig. 2. Packing of the molecules viewed down *a*.

twist leading to a more stable conformation, whereby steric interaction is reduced. In the absence of the calculations of the potential energy taking into account the contributions discussed earlier, it is not possible to isolate the steric and conjugation effects towards the twist and lengthening of the ethylene bond. It was not possible to measure the barrier to rotation about the ethylene bond for this molecule from NMR studies (Sandström & Wennerbeck, 1978).

Rotation about the double bond does not remove the steric interactions completely. The S...C(6) non-bonded distance is 3.130 (4) Å whereas the sum of the relevant van der Waals radii is 3.5 Å. Also the S...C(3) non-bonded distance is 2.886 (4) Å and the expected value is 3.2 Å. Atom C(4) deviates from the plane defined by S, N(1) and C(5) by 0.02 Å whereas C(5) deviates by 0.07 Å from the plane defined by C(4), C(6) and C(7). The torsion angles C(5)–C(7)–C(8)–C(13) and C(5)–C(7)–C(8)–C(9) are  $-51.1(5)$  and  $135.6(4)^\circ$  respectively. This is necessary in order to avoid the interaction between phenyl H atoms and the cyanide group. It is noteworthy that C(7) deviates from the plane of the phenyl ring by 0.18 Å. The  $-C-C\equiv N$  fragment is significantly non-linear [ $178.2(4)^\circ$ ].

Packing of the molecules in the unit cell as viewed down *a* is given in Fig. 2. Each molecule is surrounded by six molecules and the crystal structure is stabilized by van der Waals interactions. There are no unreasonable intermolecular distances.

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