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Polarized Twisted Ethylenes: Structures of 3-[Bis(dimethylamino)methylene]-3-phenyl-2-propanone (I), $C_{14}H_{20}N_2O$, and Methyl 2-[Bis(dimethylamino)methylene]-3-oxobutyrate Trihydrate (II), $C_{10}H_{18}N_2O_3.3H_2O$

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Abstract. (I): $M_r = 232$, orthorhombic, *Pbca*, $Z = 8$, $a = 8{\cdot}605$ (2), $b = 14{\cdot}845$ (3), $c = 21{\cdot}445$ (4) Å, $V = 2739{\cdot}4$ Å^3, $D_m = 1{\cdot}12$, $D_x = 1{\cdot}124$ g cm^{-3} (by flotation in KI solution), λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 4{\cdot}91$ cm^{-1}, $F(000) = 1008{\cdot}0$, $T = 293$ K. (II): $M_r = 268$, triclinic, $P\bar{1}$, $Z = 2$, $a = 6{\cdot}872$ (1), $b = 8{\cdot}707$ (1), $c = 12{\cdot}341$ (1) Å, $\alpha = 91{\cdot}1$ (1), $\beta = 92{\cdot}8$ (1), $\gamma = 100{\cdot}5$ (2)°, $V = 724{\cdot}9$ Å^3, $D_m = 1{\cdot}22$, $D_x = 1{\cdot}227$ g cm^{-3} (by flotation in KI solution), λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 5{\cdot}32$ cm^{-1}, $F(000) = 232{\cdot}0$, $T = 293$ K. Both structures were solved by direct methods and refined to $R = 5{\cdot}7\%$ (1563 significant reflections) for (I) and $R = 5{\cdot}5\%$ (1960 significant reflections) for (II). The C=C bond length is 1·409 (4) Å in (I) with a DNMR rotational barrier of 41·2 kJ mol^{-1}. In (II) the C=C bond length is 1·461 (2) Å with rotational barrier < 34 kJ mol^{-1}. The molecules are twisted about the C=C bond by 34·8 (3)° in (I) and 56·9 (2)° in (II). A correlation between rotational barriers (DNMR studies) and C=C bond lengths (X-ray measurements) is indicated.

Introduction. In this paper we report our findings on the molecular geometries of (I) and (II) to further our continued interest in the structure and conformation of polarized, twisted ethylenes (Adhikesavalu & Venkatesan, 1981, 1982, 1983*a*,*b*). Samples of (I) and (II) were provided by Professor Jan Sandström, University of Lund, Sweden.

Experimental. Single crystals of (I) obtained from cyclohexane by slow evaporation and those of (II) from acetone by cooling at 268 K, approximate dimensions 0·5 × 0·3 × 0·2 mm (I) and 0·6 × 0·3 × 0·2 mm (II). Preliminary Weissenberg photographs indicated orthorhombic (I) and triclinic (II) symmetry. Lattice parameters from a least-squares fit to the settings for 25 accurately centred reflections for both (I) and (II). Nonius CAD-4 diffractometer, graphite-monochromated Cu $K\alpha$ radiation, $\omega/2\theta$ scan mode, scan speed of 1° min^{-1}, $\theta \leq 60°$ (for I and II). Two monitored standard reflections ($\bar{1}57$ and $\bar{2}66$) for (I) and three ($\bar{1}\bar{2}\bar{6}$, 500 and 408) for (II) showed only statistical variations, within ±2%. 2436 (I) and 2243 (II) total reflections of which 1563 (I) and 1960 (II) were significant, $|F_o| \geq 3\sigma(|F_o|)$. No correction for absorption. Structures solved by direct methods [*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 $R = 0{\cdot}057$, $R_w = 0{\cdot}066$, $S = 1{\cdot}57$ for (I) and $R = 0{\cdot}055$, $R_w = 0{\cdot}067$, $S = 2{\cdot}96$ for (II); $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 1{\cdot}6995/[\sigma^2(F) + 0{\cdot}002278 \times |F_o|^2]$ for (I) and $w = 35{\cdot}4083/[\sigma^2(F) + 0{\cdot}024732 \times |F_o|^2]$ for (II). *SHELX*76 (Sheldrick, 1976) used for full-matrix refinement. Δ/σ for non-hydrogen atoms for (I) ~0·05 and for (II) ~0·01. Final difference maps of (I) and (II) featureless. In (II), ten strong low-angle reflections were corrected for secondary-extinction effects using the relation proposed by Darwin (1922), $I_{\rm corr} = I_o\ (1+2gI_c)$ with $g = 0{\cdot}46 \times 10^{-5}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. A perspective view and the numbering scheme with bond lengths and angles for non-hydrogen atoms for compounds (I) and (II) are shown in Figs. 1 and 2 respectively. Positional coordinates of non-hydrogen atoms of (I) and (II) are provided in Tables 1 and 2 respectively.* Table 3 gives some important torsion angles.

The C=C bond lengths of (I) [1·409 (4) Å] and (II) [1·461 (2) Å] are significantly longer than the value for this bond in ethylene [1·336 (2) Å; Bartell, Roth, Hollowell, Kuchitsu & Young (1965)] – a consequence of the donor and acceptor substituents at the C=C bond. The twist angle about the C=C bond as

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* Lists of structure factors, anisotropic thermal parameters, H-atom positions and their isotropic temperature factors and bond lengths and angles involving H atoms for (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP39051 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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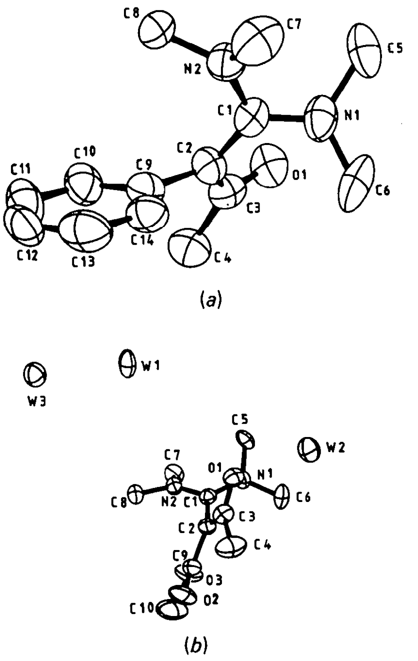


Fig. 1. Perspective views of (*a*) molecule (I) and (*b*) molecule (II).

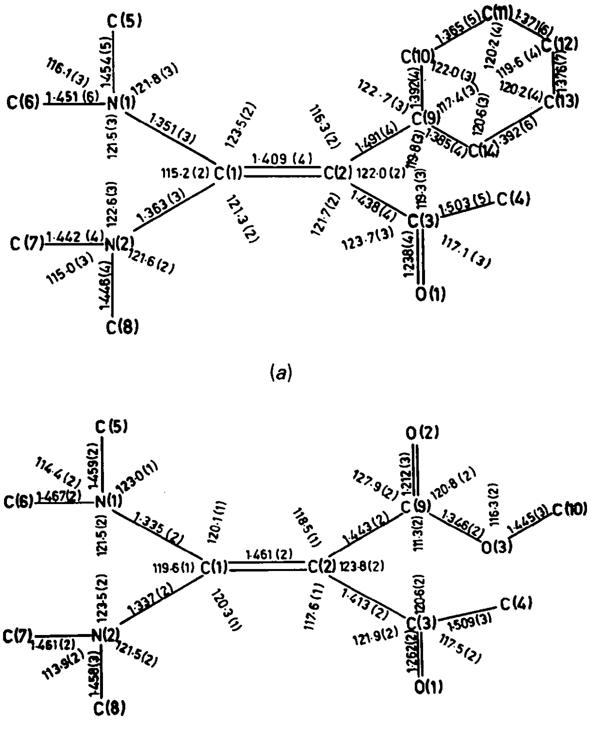


Fig. 2. Bond lengths (Å) and angles (°) of non-hydrogen atoms with their numbering schemes for (*a*) molecule (I) and (*b*) molecule (II). (E.s.d.'s are given in parentheses.)

Table 1. *Final positional parameters for nonhydrogen atoms* (× 10^4) *with equivalent isotropic temperature factors* (× 10^2) *for* (I)

E.s.d.'s are given in parentheses. $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	U_{eq}(Å^2)
N(1)	369 (3)	1333 (1)	6602 (1)	5·65 (8)
N(2)	1656 (3)	72 (1)	6938 (1)	5·06 (8)
C(1)	451 (3)	424 (2)	6606 (1)	4·52 (8)
C(2)	−594 (3)	−135 (2)	6280 (1)	4·71 (8)
C(3)	−2211 (3)	91 (2)	6219 (1)	5·20 (9)
C(4)	−3198 (5)	−418 (4)	5760 (2)	7·41 (14)
O(1)	−2853 (2)	697 (1)	6520 (1)	6·37 (8)
C(9)	69 (3)	−975 (2)	6007 (1)	5·04 (9)
C(10)	−574 (4)	−1822 (2)	6112 (2)	6·36 (11)
C(11)	79 (5)	−2589 (2)	5877 (2)	7·74 (14)
C(12)	1421 (6)	−2542 (3)	5534 (2)	8·85 (16)
C(13)	2097 (6)	−1717 (3)	5424 (2)	8·24 (15)
C(14)	1411 (4)	−934 (3)	5652 (1)	6·33 (12)
C(5)	809 (6)	1867 (3)	7142 (2)	8·21 (16)
C(6)	−376 (5)	1817 (3)	6096 (3)	8·06 (16)
C(7)	3190 (4)	462 (3)	6933 (2)	7·47 (14)
C(8)	1551 (5)	−804 (2)	7230 (2)	6·25 (12)

Table 2. *Final positional parameters for nonhydrogen atoms* (× 10^4) *with equivalent isotropic temperature factors* (× 10^2) *for* (II)

E.s.d.'s are given in parentheses. $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a^*_ia^*_j\mathbf{a}_i.\mathbf{a}_j$.

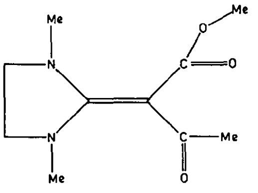
	x	*y*	*z*	U_{eq}(Å^2)
N(1)	−1689 (2)	4152 (2)	2920 (1)	3·47 (5)
N(2)	−2246 (2)	1473 (2)	2650 (1)	3·53 (5)
C(1)	−1263 (2)	2890 (2)	2421 (1)	3·08 (5)
C(2)	280 (3)	3058 (2)	1637 (1)	3·53 (5)
C(9)	−238 (3)	2440 (2)	545 (1)	4·24 (6)
O(2)	871 (3)	2241 (2)	−157 (1)	6·66 (6)
O(3)	−2217 (2)	2081 (2)	357 (1)	5·50 (5)
C(10)	−2914 (5)	1355 (4)	−687 (2)	7·75 (11)
C(3)	2190 (2)	3863 (2)	1987 (1)	3·79 (6)
O(1)	2640 (2)	4248 (2)	2972 (1)	4·47 (5)
C(4)	3762 (3)	4317 (4)	1182 (2)	6·16 (8)
C(5)	−2399 (3)	4135 (2)	4015 (2)	4·40 (7)
C(6)	−1102 (3)	5719 (2)	2492 (2)	4·86 (8)
C(7)	−4289 (3)	1181 (3)	2982 (2)	4·78 (7)
C(8)	−1497 (4)	59 (2)	2378 (2)	4·94 (8)
W(1)	8244 (2)	1078 (2)	5659 (1)	6·05 (6)
W(2)	4725 (2)	7185 (2)	3748 (1)	5·35 (6)
W(3)	7963 (2)	−2181 (2)	5291 (1)	4·96 (5)

Table 3. *Important torsion angles* (°) *with e.s.d.'s in parentheses*

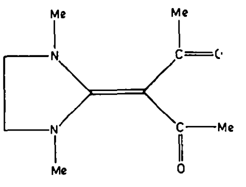
	(I)	(II)
N(1)—C(1)—C(2)—C(3)	−36·0 (4)	55·7 (2)
N(1)—C(1)—C(2)—C(9)	144·4 (3)	−122·4 (2)
N(2)—C(1)—C(2)—C(3)	145·8 (3)	−123·8 (2)
N(2)—C(1)—C(2)—C(9)	−33·8 (4)	58·1 (2)
C(2)—C(1)—N(1)—C(5)	146·6 (3)	−149·2 (2)
C(2)—C(1)—N(1)—C(6)	−24·1 (4)	18·4 (2)
C(2)—C(1)—N(2)—C(7)	138·3 (3)	−150·4 (2)
C(2)—C(1)—N(2)—C(8)	−30·6 (4)	17·0 (2)
C(1)—C(2)—C(3)—C(4)	167·3 (3)	−169·8 (2)
C(1)—C(2)—C(3)—O(1)	−11·7 (4)	9·2 (2)
C(1)—C(2)—C(9)—O(2)	—	−167·0 (2)
C(1)—C(2)—C(9)—O(3)	—	13·2 (2)
C(1)—C(2)—C(9)—C(10)	128·1 (3)	—
C(1)—C(2)—C(9)—C(14)	−49·4 (4)	—

measured by the angle between the planes N(1), C(1) and N(2) and C(9), C(2) and C(3) is 34·8 (3)° for (I) and 56·9 (2)° for (II).

It is interesting to note that in the push–pull ethylenes with cyclic donors such as in methyl 2-(1,3-dimethyl-2-imidazolidinylidene)-3-oxobutyrate dihydrate (III) (Adhikesavalu & Venkatesan, 1983*b*) and in 3-(1,3-dimethyl-2-imidazolidinylidene)-2,4-pentanedione (IV) (Adhikesavalu & Venkatesan, 1982) the C=C bond lengths are 1·464 (2) and 1·468 (3) Å respectively, the twist angles about the C=C double bond being 62·6 (3)° (III) and 72·9 (3)° (IV).



(III)



(IV)

The effect of replacing the strong acceptor methoxycarbonyl group of (II) by a phenyl group in (I), a relatively poor acceptor, is seen in the shorter C=C length in (I).

There are important changes in the bond lengths due to conjugation. The N(1)–C(1) and N(2)–C(1) in (I) [1·351 (3) and 1·363 (3) Å] and (II) [1·335 (2) and 1·337 (2) Å] respectively are shorter than 1·452 (2) Å reported for an $\ddot{N}$–C(sp^2) single bond (Ammon, Mazzocchi, Regan & Colicelli, 1979).

On the acceptor side the C(2)–C(3) bond length [1·438 (4) Å] in (I), C(2)–C(3) [1·413 (2) Å] and C(2)–C(9) [1·443 (2) Å] in (II) are much shorter than 1·487 (5) Å reported for a C(sp^2)–C(sp^2) single bond (Shmueli, Shanan-Atidi, Horwitz & Shvo, 1973).

It is noteworthy that the barrier to rotation about the C=C bond as measured from DNMR studies is larger in (I) (41·2 kJ mol^{-1}) than in (II) (< 34 kJ mol^{-1}) (Wennerbeck & Sandström, 1972). The C=C bond lengths (in Å) and the rotational barriers (kJ mol^{-1}) in some related compounds are: 3,3-bis(dimethylthio)-2-nitro-2-propene-1-nitrile, 1·376 (4) (Kamath & Venkatesan, 1983), 80·2 (Dreier, Henriksen, Karlsson & Sandström, 1978); 3-(1,3-dimethyl-2-imidazolidinylidene)-2-phenyl-2-propene-1-nitrile, 1·415 (8) (Kamath & Venkatesan, 1983), 39·9 (Sandström, Sjostrand & Wennerbeck, 1977); [dimethylamino-(methylthio)methylene]malononitrile, 1·397 (8) (Adhikesavalu & Venkatesan, 1983*a*), 55·4 (Sandström & Wennerbeck, 1978); 2-*p*-bromobenzoyl-1,3-dimethyl-4-imidazolidinylideneacetonitrile, 1·448 (4) (Abrahamsson, Rehnberg, Liljefors & Sandström, 1974), 39·9 (for the bromine-free 1,3-dibenzyl analogue) (Sandström & Wennerbeck, 1971); 2-*p*-bromobenzoyl-3,3-bis(methylthio)-2-propene-1-nitrile, 1·369 (7) (Abrahamsson *et al.*, 1974), 79·8 (bromine-free analogue) (Sandström & Wennerbeck, 1970); and 3-[bis(dimethylamino)methylene]-3-phenyl-2-propanone, 1·409 (4) (I) (present work), 41·2 (Wennerbeck & Sandström, 1972).

The donor and acceptor groups being different in these molecules, the intramolecular steric strain will be different. However, there is a remarkable correlation between C=C bond length and rotational barrier – a larger value for the rotational barrier being associated with a shorter C=C bond length.

The out-of-plane bending at C(1) and C(2) was calculated using the method described by Winkler & Dunitz (1971). In molecules (I) and (II) the values of χ_{C1} are 1·9 (4)° and 0·5 (2)° respectively and χ_{C2} values are 0·4 (4)° (I) and 1·8 (2)° (II).

The packing of the molecules in (I) is displayed in Fig. 3. There are no intermolecular short contacts. The packing of the molecules in (II) is shown in Fig. 4. The crystal structure in (II) is stabilized by a three-dimensional network of hydrogen bonds. The hydrogen-bond parameters are recorded in Table 4. There are three water molecules in the asymmetric unit. O(1) is hydrogen bonded to two water molecules (*W*2 and *W*3). Each water molecule has three neighbours at hydrogen-bonding distances.

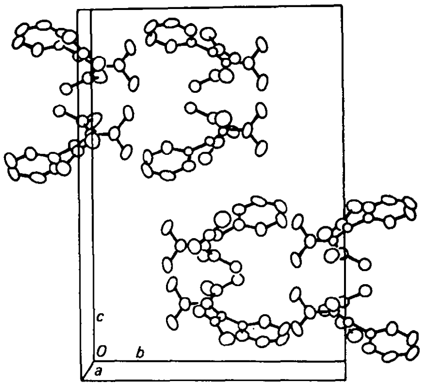


Fig. 3. Packing of molecules (I) viewed down **a**.

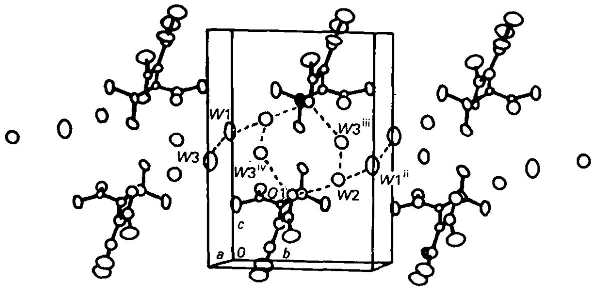


Fig. 4. Packing of molecules (II) viewed down **a**.

Table 4. *Hydrogen-bond parameters in* (II)

	$D\cdots A$(Å)	$H\cdots A$(Å)	D–H(Å)	H–$D\cdots A$(°)	D–H$\cdots A$(°)
$W(1)$–H$W(11)\cdots W(3)$	2·835 (2)	2·07 (3)	0·76 (3)	4 (2)	174 (3)
$W(1)$–H$W(12)\cdots W(3^{i})$	2·920 (2)	1·91 (5)	1·03 (5)	8 (2)	168 (4)
$W(2)$–H$W(21)\cdots$O(1)	2·819 (2)	1·97 (3)	0·85 (3)	2 (2)	177 (3)
$W(2)$–H$W(22)\cdots W(1^{ii})$	2·865 (2)	1·87 (5)	1·02 (5)	9 (3)	166 (4)
$W(3^{iii})$–H$W(31)\cdots W(2)$	2·824 (2)	1·94 (3)	0·91 (3)	12 (2)	163 (3)
$W(3^{iv})$–H$W(32)\cdots$O(1)	2·824 (2)	2·03 (3)	0·79 (3)	0 (3)	180 (3)

Symmetry code: none x, y, z; (i) $2-x, -y, 1-z$; (ii) $1-x, 1-y, 1-z$; (iii) $x, 1+y, z$; (iv) $1-x, -y, 1-z$.

$W(1)$ deviates by 0·215 (1) Å from the plane through its three hydrogen-bonded neighbours, $W(2)$ deviates 0·781 (1) Å and $W(3)$ 2·119 (2) Å. [The illustrations were made with *ORTEP*II (Johnson 1976).]

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N,*N'*-Bis(2-methylphenyl)guanidine, $C_{15}H_{17}N_3$

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Abstract. $M_r = 239{\cdot}32$, orthorhombic, *Pcab* {non-standard setting of *Pbca*, equivalent positions $\pm[x, y, z; \frac{1}{2}-x, y, \frac{1}{2}+z; \frac{1}{2}+x, \frac{1}{2}-y, z; x, \frac{1}{2}+y, \frac{1}{2}-z]$}, $a = 21{\cdot}558$ (12), $b = 13{\cdot}588$ (10), $c = 8{\cdot}980$ (5) Å, $V = 2630{\cdot}51$ Å^3, $Z = 8$, $D_m = 1{\cdot}218$ (1), $D_x = 1{\cdot}208$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 0{\cdot}62$ mm^{-1}, $F(000) = 1024$, $T = 295$ K, $R = 0{\cdot}053$ for 1245 observed [$I > 3\sigma(I)$] reflexions. The material was supplied by Imperial Chemical Industries Limited (Organics Division) under the trade name 'Vulcafor DOTG'. Molecules in the crystal are linked in chains along **c** by N—H$\cdots$N hydrogen bonds.

Introduction. The title compound is widely used as an accelerator in the curing of rubber and, as there is a scarcity of structural information on guanidine compounds, the structure determination was undertaken to improve our understanding of the industrial process.

Experimental. Recrystallized from ethanol, colourless acicular crystals, m.p. 451 K; density by flotation in NaI solution; crystal 2·0 × 0·5 × 0·2 mm used for obtaining intensities by the multiple-film technique, Stoe Weissenberg camera, layers $hk0 \rightarrow hk7$, and $h0l$ which was used for inter-layer scaling; lattice parameters

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