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Studies in Nonlinear Optical Materials: Structure of 3-Menthyl 2-[Bis(dimethylamino)methylene]-3-oxobutyrate Hemihydrate

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Abstract. $C_{19}H_{34}N_2O_3 \cdot \frac{1}{2}H_2O$, $M_r = 347.5$, monoclinic, $C2$, $a = 15.473$ (3), $b = 6.963$ (2), $c = 20.708$ (4) Å, $\beta = 108.2$ (2)°, $V = 2119$ (2) Å³, $Z = 4$, $D_x = 1.089$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 0.523$ mm⁻¹, $F(000) = 760.0$, $T = 293$ K, $R = 0.068$ for 1967 unique reflections. The C=C bond length is 1.447 (6) Å, significantly longer than in ethylene, 1.336 (2) Å. The crystal structure is stabilized by O—H...O hydrogen bonding. Explanation for the observed low second-harmonic-generation efficiency (0.5 times that of urea) is provided.

Introduction. Among the various driving forces stimulating interest in nonlinear optical materials is the development of 'all-optical devices' suitable for optical communication or optical signal processing components which permit longer band width or shorter switching times than are achieved with their electronic counterparts (Williams, 1984). In the search for new nonlinear optical materials, organic molecular crystals are of particular interest due to the extremely large variety of compounds that can be investigated for practical applications satisfying the stringent requirement (Tweig & Jain, 1983; Zyss, 1982). Systematic studies have shown that substituted aromatic molecules may exhibit very large optical nonlinearities especially if suitable donors and acceptors are bonded

to the molecular framework. For example, 2-methyl-4-nitroaniline shows exceptionally large second-harmonic nonlinear optical susceptibility (Lipscomb, Garito & Narang, 1981). Of the many potential applications of organic materials to optics technology, the one aspect the present authors have chosen to concentrate upon is the development of systems exhibiting large second-harmonic generation (SHG). In this phenomenon, light with large intensity, as with laser light, with a fundamental frequency ω interacts with the material in such a way that efficient conversion to 2ω takes place. The necessary conditions to be satisfied are (i) the crystals must be noncentrosymmetric and (ii) the molecule should have loosely bound electrons that can be displaced by the optical field. Earlier crystallographic studies on the structures of a large number of push-pull ethylenes with donor and acceptor groups in the vicinal positions of the ethylene have shown considerable delocalization of π electrons from the donor to the acceptor across the ethylene bond (Adhikesavalu, Kamath & Venkatesan, 1983). Indeed the C=C bond length in one case is observed to be as large as 1.468 (3) Å (Adhikesavalu & Venkatesan, 1983a). It appeared to us that push-pull ethylenes could be a promising system for second-order nonlinear effects. A programme of research has been initiated by us to develop suitably substituted push-pull

ethylenes as nonlinear optical materials. However, many of the push-pull ethylenes reported previously (Adhikesavalu, Kamath & Venkatesan, 1983) crystallize in centrosymmetric space groups which leads to their second-order nonlinear susceptibility being zero. This problem may be circumvented by adding a chiral group to the basic molecular skeleton either at the donor end or at the acceptor end. The title compound was synthesized by us following the reported procedure (Ericsson, Sandström & Wennerbeck, 1970) using 1-methyl 3-oxobutyrate instead of methyl 3-oxobutyrate. The SHG of the powder sample was kindly measured for us by Eaton & Wang and the intensity ratio was found to be 0.5 compared to urea.

Experimental. Single crystals of the compound were grown from a benzene-xylene solution by slow evaporation. The crystal used for the X-ray study had dimensions $0.19 \times 0.18 \times 0.40$ mm. Preliminary oscillation and Weissenberg photographs indicated the crystal to be triclinic. The presumed optical purity of the compound requires the space group to be $P1$ with $Z = 2$. The data were collected in the triclinic system. Lattice parameters refined by least-squares fit to settings of 23 accurately centered reflections in the range $7 < \theta < 28^\circ$. The intensities of 4639 reflections to a 2θ value of 154° were measured using a Nonius CAD-4 diffractometer and graphite-monochromated Cu $K\alpha$ radiation. $h: 0 \rightarrow 8$, $k: -10 \rightarrow 10$, $l: -24 \rightarrow 24$. The $\omega/2\theta$ scan mode with a 1° min^{-1} scan rate was used. Two standard reflections (013 and 105) showed little or no decay throughout the data collection. Data corrected for Lorentz and polarization factors but not for absorption.

The normalized structure factors were calculated using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The cumulative probability distribution showed that the $0kl$ reflections have centric distribution. Innumerable attempts to solve the structure using *MULTAN80* (Main *et al.*, 1980) and *SHELX76* (Sheldrick, 1976) were not successful.

In the unsuccessful attempts the convergence had chosen one origin-defining reflection (ODR) out of three and five starting-set reflections (SSR) out of seven as $0kl$ reflections, which have centric distribution. The enantiomorph was also fixed by a $0kl$ ($03\bar{3}$) reflection. Starting from these reflections, *MULTAN* produced 65 sets of phases. The E map computed for many of these sets did not reveal the structure and the maps computed contained a large 'uranium' peak. It may be mentioned that the density of the crystals could not be measured because they slowly dissolve in all solvents including water. As a benzene-xylene mixture was used for crystallization, it was suspected that the crystals contained some solvent of crystallization. With the assumption that two molecules of benzene were present

in the lattice, an attempt was made to solve the structure in $P1$, but it was to no avail. In the next attempt two xylene molecules were introduced instead of benzene and 453 reflections with $|E| \geq 1.522$ were input to the program. To our surprise, the E map computed from the best set of phases (ABSFOM=1.0832, PSIZERO=1.536, RESID=24.5, CFOM=2.3104) revealed 43 non-H atoms out of 48. The 43 non-H atoms were input to the Karle recycling procedure (Karle, 1968) and after two cycles of phase refinement all 48 non-H atoms were located ($R_{\text{Karle}} = 25.7\%$). The two independent molecules are related by a twofold axis in the (100) plane at $y = 0.35$; $z = 0.68$. A difference Fourier map with these atoms revealed only a single peak with a height of $3.8 \text{ e } \text{Å}^{-3}$. From intermolecular distances it was reasonable to identify this as a water molecule. Contrary to our expectations, there was no indication for the existence of xylene molecules, the introduction of which turned out to be the rate-determining step in the structure solution.

The structure was refined in triclinic space group $P1$ to $R = 0.067$ for 2889 reflections. A referee pointed out that the real space group could be $C2$. It is worth recalling that it has been discovered that a number of published crystal-structure determinations have been performed with space groups of incorrectly low symmetry (Marsh & Schomaker, 1981; Marsh & Herbstein, 1983; Jones, 1984; Baur & Tillmanns, 1986).

The intensity data were suitably transformed to the monoclinic system using the transformation matrix $1\bar{2}0/0\bar{1}0/01\bar{1}$ and the coordinates were subjected to least-squares refinement after transforming to the C -centered monoclinic unit cell and symmetrized about the twofold axis at (0.0, 1.0, 0.0). Full-matrix least-squares refinement of a scale factor, positional and anisotropic thermal parameters of non-H atoms and positional and isotropic thermal parameters of H atoms (27 H's located from the difference map and the rest were calculated) converged at $R = 0.068$, $wR = 0.085$ for 1967 significant reflections, $|F_o| \geq 3\sigma|F_o|$. The slightly larger value of wR may be partly due to an unsatisfactory weighting scheme. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 0.7325 \times [\sigma^2(F) + 0.002|F|^2]$; $S = 0.12$; max. Δ/σ for non-H atoms 0.058; $\Delta\rho_{\text{max}} = +0.26$, $\Delta\rho_{\text{min}} = -0.35 \text{ e } \text{Å}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). It may be noted that many attempts at structure determination *via* *MULTAN80* in the $C2$ space group were futile.*

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43956 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) for non-H atoms; *e.s.d.'s* are given in parentheses

	The temperature factor is of the form			
	x	y	z	U_{eq}
N(1)	1831 (2)	3954 (5)	793 (1)	42 (1)
N(2)	3393 (2)	4299 (6)	1161 (1)	46 (1)
O(1)	1622 (2)	8157 (5)	742 (1)	55 (1)
O(2)	3070 (3)	7246 (6)	2823 (1)	68 (1)
O(3)	3207 (2)	4189	2524 (1)	45 (1)
C(1)	2573 (2)	4820 (6)	1194 (2)	39 (1)
C(2)	2496 (2)	6321 (6)	1657 (2)	41 (1)
C(3)	1973 (2)	7953 (6)	1381 (2)	43 (1)
C(4)	1799 (3)	9539 (8)	1821 (2)	59 (1)
C(5)	1766 (3)	3110 (7)	127 (2)	54 (1)
C(6)	954 (3)	4117 (8)	916 (2)	57 (1)
C(7)	3608 (3)	2345 (8)	998 (2)	64 (1)
C(8)	4169 (3)	5580 (8)	1410 (2)	57 (1)
C(9)	2949 (3)	6025 (7)	2383 (2)	45 (1)
C(10)	3575 (3)	3628 (6)	3239 (2)	48 (1)
C(11)	2776 (3)	3381 (7)	3521 (2)	54 (1)
C(12)	3077 (3)	2576 (8)	4244 (2)	61 (1)
C(13)	3602 (3)	752 (8)	4265 (2)	64 (1)
C(14)	4399 (3)	997 (8)	3995 (2)	63 (1)
C(15)	4104 (3)	1792 (7)	3269 (2)	49 (1)
C(16)	4905 (3)	1969 (9)	2973 (2)	66 (1)
C(17)	5210 (4)	-7 (12)	2816 (3)	98 (2)
C(18)	5661 (4)	3208 (13)	3383 (3)	106 (2)
C(19)	2266 (4)	2345 (10)	4506 (3)	84 (1)
W(1)	0	10013 (7)	0	63 (1)

Discussion. The atomic positional and thermal parameters for non-H atoms are listed in Table 1. Intramolecular distances and bond angles are presented in Table 2. An ORTEP drawing (Johnson, 1976) of the molecule showing the atomic numbering scheme is illustrated in Fig. 1.

The combined effect of the strongly electron-donating *N,N*-dimethylamino groups and the electron-accepting acetyl and menthoxy carbonyl groups substituted at the vicinal C atoms of the ethylene is to produce a remarkable lengthening of the C=C bond to 1.447 (6) Å, which is significantly longer than this bond in ethylene [1.336 (2) Å; Bartell, Roth, Hollowell, Kuchitsu & Young (1965)] and is comparable within experimental error to the value of 1.461 (2) Å in methyl 2-[bis(dimethylamino)methylene]-3-oxobutrylate trihydrate (Kamath & Venkatesan, 1984). The N(1)–C(1) and N(2)–C(1) distances of 1.332 (5) and 1.342 (5) Å respectively are shorter than 1.452 (2) Å reported for an N–C(*sp*²) bond (Ammon, Mazzocchi, Regan & Colicelli, 1979).

On the acceptor side, the C(2)–C(3) bond of 1.409 (6) Å and C(2)–C(9) of 1.461 (5) Å are shorter than 1.487 (5) Å in a similar system (Shmueli, Shanan-Atidi, Horwitz & Shvo, 1973). The C(3)–O(1) bond length is 1.272 (4) Å. The lengthening of this bond may be due to conjugation as well as to the involvement of O atoms in hydrogen bonding with the water molecule. Examples are known where the C=O bond is lengthened due to hydrogen bonding (Craven,

Cusatis, Gartland & Vizzini, 1973; Ramani, Venkatesan & Marsh, 1978). The C(9)=O(2) bond of length 1.217 (5) Å is comparable to the value of 1.195 (7) Å reported for such bonds (Adhikesavalu & Venkatesan, 1983b). The C–C bond length in the cyclohexane ring varies from 1.501 (8) to 1.533 (7) Å with a mean of 1.520 (7) Å. The mean C–C–C valence angle in this

Table 2. Selected bond distances (Å) and angles (°) involving non-H atoms with their *e.s.d.'s* in parentheses

N(1)–C(1)	1.332 (5)	C(2)–C(9)	1.461 (6)
N(1)–C(5)	1.473 (5)	C(3)–C(4)	1.509 (6)
N(1)–C(6)	1.462 (6)	C(10)–C(11)	1.533 (7)
N(2)–C(1)	1.342 (5)	C(10)–C(15)	1.508 (7)
N(2)–C(7)	1.464 (7)	C(11)–C(12)	1.530 (6)
N(2)–C(8)	1.455 (6)	C(12)–C(13)	1.501 (8)
O(1)–C(3)	1.272 (4)	C(12)–C(19)	1.523 (8)
O(2)–C(9)	1.217 (5)	C(13)–C(14)	1.513 (7)
O(3)–C(9)	1.344 (5)	C(14)–C(15)	1.533 (6)
O(3)–C(10)	1.464 (4)	C(15)–C(16)	1.549 (7)
C(1)–C(2)	1.447 (6)	C(16)–C(17)	1.522 (10)
C(2)–C(3)	1.409 (6)	C(16)–C(18)	1.488 (9)
C(1)–N(1)–C(5)	123.9 (3)	O(2)–C(9)–C(2)	125.8 (4)
C(1)–N(1)–C(6)	121.4 (3)	O(3)–C(9)–C(2)	111.8 (4)
C(5)–N(1)–C(6)	113.5 (3)	O(3)–C(10)–C(11)	108.0 (3)
C(1)–N(2)–C(7)	123.3 (3)	O(3)–C(10)–C(15)	107.6 (3)
C(1)–N(2)–C(8)	120.4 (3)	C(11)–C(10)–C(15)	112.4 (4)
C(7)–N(2)–C(8)	115.4 (3)	C(10)–C(11)–C(12)	112.3 (4)
C(9)–O(3)–C(10)	118.0 (3)	C(11)–C(12)–C(13)	109.5 (4)
N(1)–C(1)–N(2)	119.3 (3)	C(11)–C(12)–C(19)	110.8 (4)
N(1)–C(1)–C(2)	120.5 (3)	C(13)–C(12)–C(19)	113.5 (4)
N(2)–C(1)–C(2)	120.2 (3)	C(12)–C(13)–C(14)	113.0 (4)
C(1)–C(2)–C(3)	118.0 (3)	C(13)–C(14)–C(15)	112.0 (4)
C(1)–C(2)–C(9)	117.8 (3)	C(10)–C(15)–C(14)	109.7 (4)
C(3)–C(2)–C(9)	124.1 (4)	C(10)–C(15)–C(16)	114.0 (4)
O(1)–C(3)–C(2)	121.1 (4)	C(14)–C(15)–C(16)	112.7 (4)
O(1)–C(3)–C(4)	116.6 (4)	C(15)–C(16)–C(17)	110.6 (4)
C(2)–C(3)–C(4)	122.3 (4)	C(15)–C(16)–C(18)	113.9 (5)
O(2)–C(9)–O(3)	122.4 (4)	C(17)–C(16)–C(18)	113.9 (5)

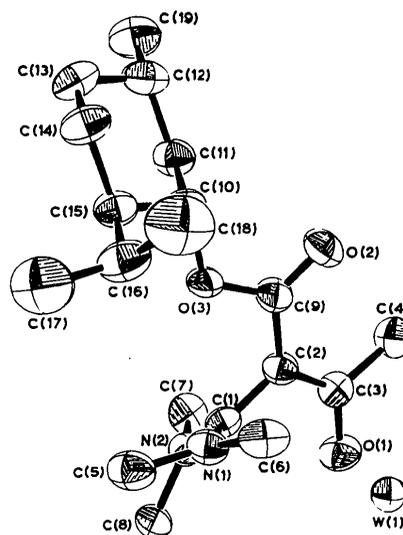


Fig. 1. ORTEP (Johnson, 1976) drawing of the molecule showing the atomic numbering scheme (50% probability ellipsoids)

ring is $111.5(4)^\circ$. The torsion angles within the cyclohexane ring are comparable to the experimental mean torsion angle of 55.9° in gaseous cyclohexane (Buys & Geise, 1970).

The observed variations in the bond lengths show that there is considerable delocalization of π electrons between the donor and acceptor groups across the ethylene bond. The single-bond character of the ethylene bond coupled with the intramolecular steric effects result in large rotation about the C(1)=C(2) bond. The angle between the plane passing through the atoms N(1), C(1), N(2) and that through C(3), C(2), C(9) is $59.3(5)^\circ$.

The packing of the molecule is displayed in Fig. 2. The crystal structure is stabilized by hydrogen bonding. The water molecule forms a hydrogen bond with the ketonic carbonyl O atom. The hydrogen-bonding parameters are $O(1)\cdots W(1) = 2.814(4)$, $O(1)\cdots H(W1) = 1.89(3)$ Å and $O(1)\cdots H(W1)-W(1) = 156(3)^\circ$.

Because of the considerable delocalization of π electrons in this molecule one would expect it to possess a strong even-order hyperpolarizability and hence good SHG efficiency. The SHG measurements carried out on the powder of the title compound (Eaton & Wang, 1986) show that the SHG efficiency is only half that of urea. A similar situation is seen in *N,N*-dimethyl-*p*-nitroaniline. In spite of its high dipole moment and crystallization in a noncentrosymmetric space group, this compound shows very low second-order efficiency because of the quasi-antiparallel molecular packing in the unit cell (Zyss, Nicoud & Coquillary, 1984; Mak & Trotter, 1965).

It is reasonable to assume in the present molecule that the polar axis of the molecule is along the C(1)=C(2) bond. The angle between the polar axis and the crystallographic twofold axis is 43.5° which is close to the theoretically calculated value of 54.7° favorable for nonlinear interactions in crystals belonging to the point group 2 (Oudar & Zyss, 1982). The observed low SHG efficiency of the title compound in comparison with urea could be due to the following. If the polar axis of the molecule is parallel to the twofold axis then the SHG efficiency would be expected to be better. The second-harmonic efficiency depends on the change in dipole moment between an excited state and

the ground state (Zyss & Berthier, 1982). It is likely that the difference in dipole moments in the title molecule is not significant.

Strategies of the kind being explored in crystal-structure engineering in solid-state photochemistry (Schmidt, 1971; Gnanaguru, Ramasubbu, Venkatesan & Ramamurthy, 1985) may be useful for achieving better nonlinear optical efficiency. In this connection, the recently reported results on the use of host-guest inclusion complexes to control the bulk nonlinear optical properties are worthy of note (Wang & Eaton, 1985; Tomaru, Zembutsu, Kawachi & Kobayashi, 1984). Wang & Eaton (1985) have observed that the conversion efficiency of the 1:1 inclusion complex between *p*-nitroaniline and β -cyclodextrin is 2–4 times that of urea. Similarly, Tomaru *et al.* (1984) have reported that the complexes of dimethyl β -cyclodextrin–nitroaniline derivatives exhibit enhanced SHG intensities. These observations have demonstrated the possibility of achieving good nonlinear optical materials using a chiral host system. But our study on the inclusion complexes of β -cyclodextrin with push–pull ethylene discussed in this paper without chiral attachment (methyl instead of menthyl) shows almost zero SHG efficiency. It seems likely that the guest molecules are randomly oriented in the host medium. Full structural elucidation of this complex with the purpose of rationalizing the experimental observation is to be undertaken in the near future.

We record our indebtedness to a referee for pointing out that the space group of the crystal should be *C*2 rather than *P*1 as originally chosen by the present authors. We thank Dr S. Ramakumar for helpful comments.

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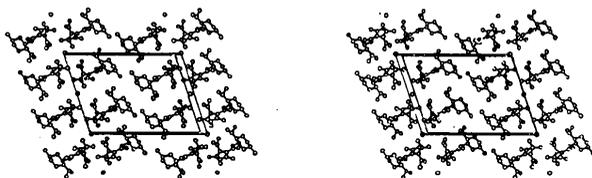


Fig. 2. Packing of the molecules viewed down the *b* axis, *c* axis horizontal.

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Structure du Chlorhydrate de la Méthyl-3 (Amino-2 Ethyl)-6 Dihydro-2,3 Benzoxazole-1,3 One-2

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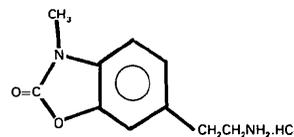
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Abstract. $C_{10}H_{13}N_2O_2^+Cl^-$, $M_r = 228.5$, triclinic, $P\bar{1}$, $a = 21.226$ (3), $b = 5.785$ (1), $c = 4.491$ (1) Å, $\alpha = 94.53$ (5), $\beta = 90.05$ (5), $\gamma = 94.92$ (5)°, $V = 556.2$ Å³, $Z = 2$, $D_x = 1.38$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 3.4$ cm⁻¹, $F(000) = 274$, $T = 298$ K, $wR = 0.055$ for 1732 independent reflexions [$I > 3\sigma(I)$]. The molecule is in an extended configuration. The crystal cohesion is enhanced by three hydrogen bonds between the Cl atom and three N atoms belonging to different molecules. The molecular conformation is compared with that of other dopaminergic or adrenergic drugs.

Introduction. La synthèse de cette nouvelle molécule a été effectuée dans le cadre d'un travail de préparation de composés susceptibles de se fixer sur les récepteurs dopaminergiques (Lesieur, Lespagnol, Caignard & Busch, 1983). Des études pharmacologiques ont montré que ce produit ne possède qu'une très faible affinité

pour ce type de récepteurs (Caignard, 1985), et qu'il se comporte, par ses propriétés cardiostimulantes, comme un agoniste des récepteurs β_1 adrénergiques (Caignard, Lespagnol, Lesieur & Busch, 1985).



La détermination de sa structure cristalline permet de comparer ses caractéristiques stériques à celles de la dopamine et de la noradrénaline.

Partie expérimentale. Echantillon monocristallin en forme de parallélépipède sensiblement rectangle (0,6 × 0,5 × 0,3 mm) préparé par évaporation lente d'une solution dans l'éthanol, paramètres de maille déterminés