Structure of *N,N*-Dimethyl-2-nitrovinylamine, C$_4$H$_8$N$_2$O$_2$

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Abstract. $M_r = 116 \cdot 11$, monoclinic, $P2_1/n$, $a = 10 \cdot 053$ (1), $b = 7 \cdot 547$ (1), $c = 7 \cdot 995$ (1) Å, $\beta = 105 \cdot 20$ (1)°, $V = 585 \cdot 3$ (1) Å^3, $Z = 4$, $D_x = 1 \cdot 31$, $D_m = 1 \cdot 30$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å, $\mu = 0 \cdot 099$ mm^{-1}, $F(000) = 248$, $T = 300$ K, final $R = 0 \cdot 070$ for 1202 observed reflections. The molecule as a whole is nearly planar and the twist angle around the C=C bond is $-179 \cdot 1$ (2)°; such conformation together with the shortening of C(1)–N(1) [$1 \cdot 390$ (3) Å] and specially of the C(2)–N(2) bond [$1 \cdot 325$ (3) Å] and significant lengthening of the C(1)=C(2) double bond [up to $1 \cdot 350$ (3) Å] can be attributed to the tendency of the ethylene bond towards conjugation with the dimethylamino and nitro moieties. Packing of the molecules is governed by normal van der Waals contacts.

Introduction. *N,N*-Dimethyl-2-nitrovinylamine (I) and compounds of related structure have been extensively investigated by use of NMR spectroscopy (Shmueli, Shanan-Atidi, Horwitz & Shvo, 1973), so the X-ray study of (CH$_3$)$_2$NCH=CHNO$_2$ was carried out in order to establish unequivocally the molecular conformation and to perform a comparison with previously determined structures, as part of studies of 'enaminones' that are planar, or nearly planar, mesomeric systems which can exist in several configurational and conformational isomeric forms, due to restriction of the rotation around the olefinic double bond and the C–N bonds.

(I)
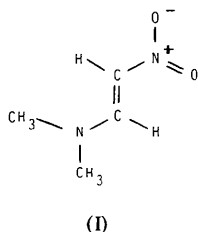
Experimental. Needle-shaped colourless crystals, approximate dimensions $0 \cdot 08 \times 0 \cdot 11 \times 0 \cdot 18$ mm, density measured by flotation. Unit-cell parameters from least-squares refinement of values of 25 reflections in range $5 < \theta < 12°$. Nonius CAD-4 diffractometer,

graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ mode, $2\theta_{max} = 60°$ ($-14 < h < 14$, $k \le 10$, $l \le 11$). Two standard reflections ($\bar{3}\bar{1}2$ and 004) monitored every 100 reflections showed only statistical fluctuations, 1722 independent reflections measured, 1202 intensities with $I \ge 2\sigma(I_o)$ considered as observed and used for the structure determination; corrections for Lorentz and polarization, absorption and extinction ignored. Structure solved by direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); 314 E values ($E > 1 \cdot 35$) used as input to *MULTAN* and the correct set with the highest figure of merit of $2 \cdot 38$ and residual value of $16 \cdot 97$ gave approximate positions of the eight non-H atoms. Scattering factors from *International Tables for X-ray Crystallography* (1962), full-matrix least-squares refinement of non-H atoms with isotropic temperature factors and unit weights gave $R = 0 \cdot 14$; with anisotropic temperature factors and weighting scheme $w = 1/\sigma^2(F)$ R dropped to $0 \cdot 11$. Difference Fourier synthesis (calculated up to $\sin\theta/\lambda = 0 \cdot 7$ Å^{-1}) revealed positions of all H atoms. Further refinement on F with non-H atoms treated anisotropically and H atoms isotropically produced convergence with $R = 0 \cdot 07$, $wR = 0 \cdot 053$ and $S = 4 \cdot 5$. In final cycle H atoms were assigned isotropic thermal parameters equal to those of bonded C atoms. Final difference Fourier synthesis showed $\Delta\rho = \pm 0 \cdot 35$ e Å^{-3}. Max. least-squares shift to error $= 0 \cdot 05$. *XRAY*70 system (Stewart, Kundell & Baldwin, 1970) of computer programs used.

Discussion. Positional and equivalent isotropic thermal parameters for the non-H atoms are given in Table 1.* Bond lengths and angles are given in Fig. 1, which shows a view of the molecule.

The molecule as a whole is approximately planar with maximum deviation of $0 \cdot 035$ (3) Å of non-H atoms from the mean-squares plane determined by all

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non-H atoms. The experimental results indicate that the stereochemistry of the C(1)=C(2) bond is
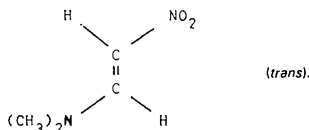
The N(1)—C(1) and N(2)—C(2) bond distances of 1·390 (3) and 1·325 (3) Å indicate partial double-bond character and the fact that the N(1) and N(2) atoms are coplanar with the three atoms bonded to them [deviations of N(1) and N(2) from the corresponding plane −0·004 (2) and −0·020 (2) Å] indicates that the state of hybridization of the two N atoms is sp^2. The C=C bond length is 1·350 (3) Å [normal double bond in ethylene 1·336 (2) Å, Bartell, Roth, Hollowell, Kuchitsu & Young (1965)] and the twist angle around this bond is −179·1 (2)°. The N(1)—O(11) and N(1)—O(12) bond distances in the nitro group are 1·236 (3) and 1·250 (3) Å. The bond angle O(11)—N(1)—O(12) of 120·0 (2)° is in agreement with the corresponding angle in nitromalonamide (Simonsen & Thorup, 1979; Simonsen, 1981). There are no significant differences concerning the N—CH₃ distances. Thus the molecular structure cannot be expressed in a satisfactory way by a single canonical formula. Some electron delocalization can be deduced from inspection of the bond distances that could be explained by the non-integer bond orders
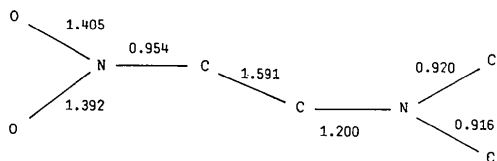

Taking into account the acceptor effect of the NO₂ group which affects the electronic configuration of the molecule, specially the C=C bond, the two forms (1) and (2) should contribute to the electronic state of the molecule.
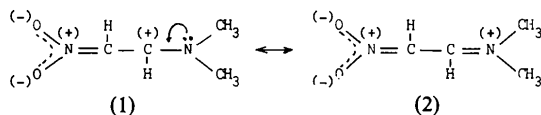
Form (1) would justify the shortening of the C(1)—N(1) and the lengthening of both the N(1)—O(12) and the N(1)—O(11) bonds with the localization of a positive charge on the N(1) atom. Form (2) is consistent with the shortening of the C(2)—N(2) distance that leaves the N(2) atom with a deficiency of charge and produces a shortening of the N(2)—C(21) and the N(2)—C(22) bonds, because this attractive effect is through a σ

bond. These canonical forms have been explained by ¹H NMR for nitrovinylindole (Subirats & Rodriguez, 1984). So the model of the molecule characterized by the π-electron densities could be
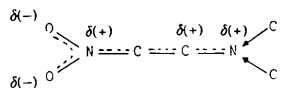
The packing in the unit cell is shown in Fig. 2. The observed arrangement is due only to van der Waals interactions.

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

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a^*_i a^*_j \cdot \mathbf{a}_i \cdot \mathbf{a}_j \cos(a_i a_j).$$

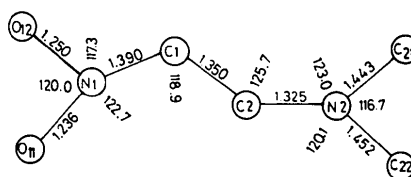|	x	y	z	U_{eq}
N(1)	8779 (2)	7736 (3)	2497 (3)	619 (8)
N(2)	8738 (2)	6063 (3)	6722 (2)	533 (6)
C(1)	9214 (3)	7476 (3)	4279 (3)	565 (8)
C(2)	8462 (2)	6416 (3)	5042 (3)	529 (8)
C(21)	9936 (3)	6744 (4)	7973 (4)	668 (10)
C(22)	7881 (3)	4825 (4)	7363 (4)	717 (11)
O(11)	7742 (2)	7013 (3)	1572 (2)	819 (8)
O(12)	9495 (2)	8731 (3)	1833 (3)	873 (9)

Fig. 1. Interatomic distances (Å) and angles (°). Mean standard deviations are 0·003 Å in distances and 0·2° in angles.
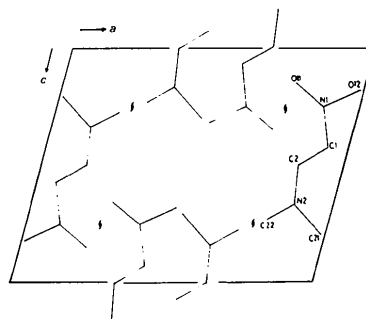

Fig. 2. The molecular packing viewed along the y axis.

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19-(p-Bromophenyl)-12-methoxypodocarpa-8,11,13-trien-19-one,* $C_{24}H_{27}BrO_2$

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Abstract. $M_r = 427.386$, monoclinic, $P2_1$, $a = 7.830$ (1), $b = 19.049$ (5), $c = 7.361$ (1) Å, $\beta = 104.34$ (1)°, $V = 1063.7$ Å^3, $Z = 2$, $D_m = 1.32$, $D_x = 1.33$ Mg m^{-3}, $\lambda(Mo\,K\alpha) = 0.7107$ Å, $\mu = 18.82$ mm^{-1}, $F(000) = 444$, room temperature. Final $R = 0.0451$ for 1660 observed $[I > 2\sigma(I)]$ reflections. The structure of the diterpene shows ring A in a chair and ring B in a half-chair conformation. The aromatic ring, C, has a methoxy substituent at C(12). The carbonyl oxygen of the 4β-axial aryl carbonyl substituent is twisted out of the plane of the adjacent phenyl ring as suggested by chemical and spectroscopic data.

Introduction. Podocarpic acid (12-hydroxypodocarpa-8,11,13-trien-19-oic acid) provides a convenient source of chiral starting material for the synthesis of complex molecules (Spencer, Smith, Storm & Villarica, 1971; Bennett, Cambie, Franich & Fullerton, 1969). Attempts to functionalize podocarpic acid derivatives at the C(10) methyl group by photolysis of attached aryl ketone groups were unsuccessful, which was attributed to steric hindrance to π-electron delocalization between the aryl and carbonyl moieties (Smith, 1983). The structure of the title compound was determined to investigate this possibility.

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* IUPAC name: *p*-bromophenyl 1,2,3,4,4a,9,10,10a-octahydro-6-methoxy-1,4a-dimethyl-1-phenanthryl ketone.

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Experimental. Crystals grown from ethanol as colourless plates, dimensions $0.48 \times 0.60 \times 0.28$ mm. Density by flotation in aqueous KI. Preliminary precession photography (Cu $K\alpha$) indicated monoclinic space groups $P2_1$ or $P2_1/m$. The non-centrosymmetric alternative was preferred for the chiral molecule and this choice was confirmed by the success of the refinement. Nicolet $P\bar{3}$ diffractometer, Mo $K\alpha$ radiation (graphite monochromator), cell dimensions determined by least squares from settings of 24 strong reflections in the range $27 < 2\theta < 29°$. Range of hkl: 10, 24, ±10, $2\theta_{max} = 52°$; max. intensity variation of 7% in standard reflections 0,10,0, 013 and 320; intensities corrected for Lorentz and polarization effects, and empirical absorption corrections applied using *SHELXTL* (Sheldrick, 1980), transmission factors 0.355–0.427. Of 2174 unique reflections ($R_{int} = 0.0095$) 1660 were considered observed with $I > 2\sigma(I)$. Structure determined by Patterson and Fourier methods, and refined by full-matrix least squares, minimizing $\sum w(|F_o| - |F_c|)^2$, using *SHELX*76 (Sheldrick, 1976). All non-hydrogen atoms assigned anisotropic thermal parameters with scattering factors from *SHELX*76. H atoms included in calculated positions (C–H = 1.08 Å) with fixed isotropic temperature factors. $w = [\sigma^2(F) + 0.0019F^2]^{-1}$. Final $R = 0.0451$, $wR = 0.0522$ for the 1660 observed reflections (the opposite enantiomorph refined to $R = 0.0531$, $wR = 0.0653$, so that the results presented here correspond to the correct absolute configuration). $(\Delta/\sigma)_{max} = 0.521$ (U_{12} for Br). The final difference map showed a maximum peak of 0.37 e Å^{-3} (0.95 Å from Br), remaining peaks < 0.20 e Å^{-3}.