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Structure of a Push–Pull Olefin: *trans*-*N*,*N*-Dimethyl-2-nitroethenamine*

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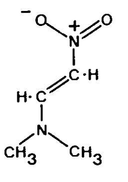
Abstract. $C_4H_8N_2O_2$, $M_r = 116{\cdot}1$, monoclinic, $P2_1/c$, $a = 8{\cdot}001$ (5), $b = 7{\cdot}562$ (4), $c = 11{\cdot}099$ (6) Å, $\beta = 118{\cdot}98$ (3)°, $V = 587{\cdot}6$ Å^3, $Z = 4$, $D_c = 1{\cdot}31$ Mg m^{-3}. The final $R = 0{\cdot}039$ for 106 parameters and 526 reflexions. The molecule is in the *trans* form although the coupling constant between the olefinic H atoms is typical for a *cis* compound.

Introduction. *N*,*N*-Dimethyl-2-nitroethenamine (I) gives an NMR spectrum typical for a *cis*-1,2-disubstituted olefin. The coupling constant between the olefinic H atoms is 10 Hz (Büchi & Mak, 1977); tabulated values (Brügel, 1967) range from 5 to 12 Hz for *cis*- and 14 to 16 Hz for *trans*-1,2-disubstituted olefins. The *cis* configuration is, however, unlikely because of steric hindrance. We have therefore determined the crystal structure to resolve the apparent paradox.



(I)

Single crystals were obtained from a solution in methanol. A crystal, 0·125 × 0·25 × 0·33 mm, was mounted on a Picker FACS-1 diffractometer. Cell dimensions were determined from the setting angles of 12 reflexions. Intensities were measured out to $2\theta = 47°$ with monochromated Mo $K\alpha$ radiation. Data were collected with the ω–2θ step-scanning technique with a step length of 0·04° and a scan width of $(2{\cdot}8 + 0{\cdot}692 \times \tan\theta)°$. Each step was counted for 1 s. 866 independent reflexions were obtained, of which 526 had $I > 3\sigma(I)$ according to counting statistics. No corrections were made for absorption.

The structure was determined with *MULTAN* (Germain, Main & Woolfson, 1971). Least-squares refinement (*LINUS*, Coppens & Hamilton, 1970) of a scale factor and atomic coordinates and anisotropic thermal parameters for the non-hydrogen atoms gave $R = 0{\cdot}087$. The H atoms were located from a difference

Table 1. *Fractional coordinates* ($\times 10^4$ *for heavy atoms*, $\times 10^3$ *for* H *atoms*), *deviations*, Δ, *from the best plane through the heavy atoms* [$\sigma(\Delta)$ *is ca* 0·002 Å *for* C, N, *and* O, *ca* 0·03 Å *for* H] *and* U_{iso} ($\times 10^3$)

	x	y	z	Δ (Å × 10^{-3})	U_{iso} (Å^2)*
O(1)	2344 (3)	8731 (3)	511 (2)	−6	80
O(2)	3831 (3)	7001 (3)	2259 (2)	−7	75
N(1)	7992 (3)	6060 (3)	1263 (2)	35	48
N(2)	3710 (3)	7734 (3)	1224 (3)	0	55
C(1)	6575 (4)	6422 (4)	1534 (3)	19	49
C(2)	5063 (4)	7474 (4)	791 (3)	−1	54
C(3)	8031 (6)	6741 (5)	57 (4)	−16	62
C(4)	9478 (5)	4815 (4)	2112 (4)	−24	68
H(1)	664 (4)	583 (4)	236 (3)	1	73 (11)
H(2)	480 (4)	808 (3)	−5 (3)	−24	62 (9)
H(31)	727 (5)	609 (4)	−74 (4)	−878	110 (14)
H(32)	767 (5)	797 (5)	−13 (3)	551	103 (13)
H(33)	938 (6)	696 (5)	26 (3)	511	113 (13)
H(41)	1075 (6)	537 (5)	238 (4)	702	107 (12)
H(42)	943 (5)	453 (5)	291 (4)	102	103 (13)
H(43)	937 (5)	370 (6)	160 (3)	−899	125 (14)

* For the non-hydrogen atoms U_{iso} is calculated from the U_{ij} by $U_{iso} = (U_1.U_2.U_3)^{2/3}$ where U_1, U_2 and U_3 are the r.m.s. amplitudes of vibration along the principal axes of the U_{ij}.

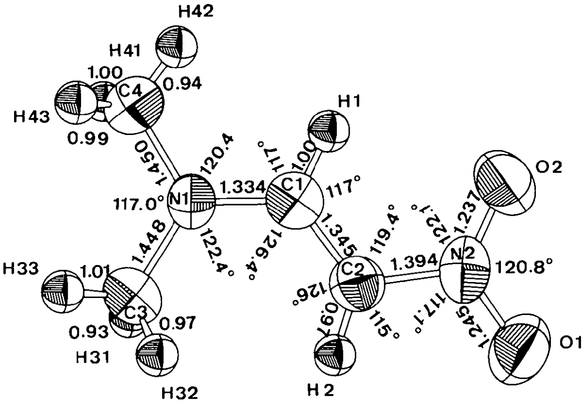


Fig. 1. Bond lengths (Å) and angles (°). The e.s.d.'s are: C—C and C—N $\sigma = 0{\cdot}004$ Å, N—O $\sigma = 0{\cdot}003$ Å, C—H $\sigma = 0{\cdot}03$ to 0·04 Å; angles not involving H have $\sigma = 0{\cdot}3°$, ∠NCH and ∠CCH $\sigma = 2°$, ∠HCH $\sigma = 3°$. The angles not shown on the figure are: N(1)–C(3)–H(31) = 113, N(1)–C(3)–H(32) = 114, N(1)–C(3)–H(33) = 111, H(31)–C(3)–H(32) = 108, H(31)–C(3)–H(33) = 116, H(32)–C(3)–H(33) = 94, N(1)–C(4)–H(41) = 108, N(1)–C(4)–H(42) = 112, N(1)–C(4)–H(43) = 111, H(41)–C(4)–H(42) = 109, H(41)–C(4)–H(43) = 109, H(42)–C(4)–H(43) = 108°.

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* Alternative name: *trans*-*N*,*N*-Dimethyl-2-nitrovinylamine.

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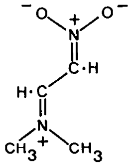
synthesis. Further refinement including the H atoms gave $R = 0·039$ and $R_w = 0·041$. In the final cycles an isotropic extinction parameter, g, was refined with the assumption that $\bar{t}$ was unity. The value of g was $7(1) \times 10^{-7}$ giving a minimum value for F_o/F_o(corrected) of 0·82. The weighting scheme was $w = \{[\sigma(F_o)^2 + 1·02F_o^2]^{1/2} - |F_o|\}^{-2}$. The scattering factors were those of Cromer & Mann (1968) for C, N and O and of Stewart, Davidson & Simpson (1965) for H.

Atomic coordinates are given in Table 1,* bond lengths and angles in Fig. 1.

Discussion. The molecule is approximately planar with the nitro and dimethylamine groups *trans*. Substitution by donor and by acceptor groups leads to a charge separation (II), the push–pull effect, resulting in the migration of the π electrons to the C—N bonds. The C—C bond is thus longer than a double bond and the C—N bonds are shorter than single bonds. In Table 2 the bond lengths are compared with those in ethylene and in some 1-substituted ethenes. The angle C(1)—C(2)—H(1) is 126 (2)°; the large deviation from 120° may be real since the corresponding angle in $H_2C:CHNO_2$ is determined by microwave spectroscopy to be 127°.



(II)

The coupling constant ^3J is, according to Lynden-Bell & Harris (1969), decreased by (*a*) electronegative substitutents, (*b*) increase of HCC angles, (*c*) increase of C—C length. It would seem that here the effects combine to give a coupling constant so low as to be characteristic of a *cis* compound. Other examples of *trans* compounds with low coupling constants do exist. *trans*-Butadiene has $J = 10·41$ Hz (Brügel, 1967), but the C—C bond is so long [1·48 (3) Å, Almenningen, Bastiansen & Trætteberg (1958)] that it can hardly be regarded as an olefin. *trans*-1,2-Difluoroethene which has strongly electronegative substituents has $J = 9·5$ Hz (Ihrig & Smith, 1972).

Table 2. *Comparison of bond lengths* (Å) *with those in some related compounds*

		$H_2C:CH_2$[a]	$H_2C:CHNO_2$[b]	$H_2C:CHNH_2$[c]
C=C	1·345 (4)	1·337 (3)	1·325 (2)	1·335*
C—NO_2	1·394 (4)	–	1·458 (1)	–
C—NR_2	1·334 (4)	–	–	1·40

References: (*a*) Allen & Plyler (1958); (*b*) Nösberger, Bauder & Günthard (1975); (*c*) Lovas, Clark & Tiemann (1975). All determined by microwave spectroscopy.

* Assumed.

The conclusion is that although the magnitudes of coupling constants can often be used to predict the configuration of 1,2-disubstituted olefins there are cases where the method is inadequate.

We are indebted to Professor K. Torssell for suggesting the problem and growing the crystals.

References

Allen, H. C. & Plyler, E. K. (1958). *J. Am. Chem. Soc.* **80**, 2673–2676.

Almenningen, A., Bastiansen, O. & Trætteberg, M. (1958). *Acta Chem. Scand.* **12**, 1221–1225.

Brügel, W. (1967). *Nuclear Magnetic Resonance and Chemical Structure*. Vol. 1. London, New York: Academic Press.

Büchi, G. & Mak, C. (1977). *J. Org. Chem.* **42**, 1784–1786.

Coppens, P. & Hamilton, W. C. (1970). *Acta Cryst.* A**26**, 71–83.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Ihrig, A. M. & Smith, S. L. (1972). *J. Am. Chem. Soc.* **94**, 34–41.

Lovas, F. J., Clark, F. O. & Tiemann, E. (1975). *J. Chem. Phys.* **62**, 1925–1931.

Lynden-Bell, R. M. & Harris, R. K. (1969). *Nuclear Magnetic Resonance Spectroscopy*. London: Nelson.

Nösberger, P., Bauder, A. & Günthard, H. H. (1975). *Chem. Phys.* **8**, 245–251.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34954 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.