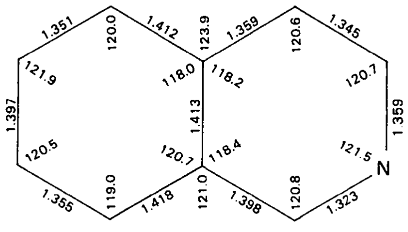

Fig. 3. Average bond distances (Å) and angles (°) in $C_9H_8N^+$.

References

Addison, C. C., Logan, N., Wallwork, S. C. & Garner, C. D. (1971). *Q. Rev. Chem. Soc.* **25**, 289–322.

Blessing, H., Coppens, P. & Becker, P. (1972). *J. Appl. Cryst.* **7**, 488–492.

Brock, C. P. & Dunitz, J. C. (1982). *Acta Cryst.* B**38**, 2218–2228.

Buranda, T., Newman, K. E. & Pinkerton, A. A. (1987). To be published.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

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

Genet, F. (1965). *Bull. Soc. Fr. Minéral. Cristallogr.* **88**, 463–482.

Johnson, C. K. (1971). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

Pinkerton, A. A. & Schwarzenbach, D. (1980). *J. Chem. Soc. Dalton Trans.* pp. 1300–1303.

Schwarzenbach, D. (1971). Abstr. 4th Eur. Crystallogr. Meet., Oxford, p. 134.

Sheldrick, G. M. (1983). *SHELXTL Users' Manual*, revision 4. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1972). The *XRAY72* system. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

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

Acta Cryst. (1987). C**43**, 1821–1822

Structure of a Substituted Butene

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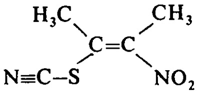
Abstract. *cis*-3-Nitro-2-thiocyanato-2-butene, $C_5H_6N_2O_2S$, $M_r = 158{\cdot}2$, monoclinic, $P2_1/c$, $a = 14{\cdot}410\,(5)$, $b = 6{\cdot}828\,(1)$, $c = 7{\cdot}581\,(2)$ Å, $\beta = 102{\cdot}63\,(2)°$, $V = 727{\cdot}89$ Å^3, $Z = 4$, $D_x = 1{\cdot}44$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 3{\cdot}8$ cm^{-1}, $F(000) = 328$, $T = 298$ K, $R = 0{\cdot}040$ for 1171 unique observed reflections with $I > \sigma(I)$. The C atoms of the butene portion, together with the S of the thiocyanate group and the N of the nitro group, form a nearly planar backbone (no atom more than 0·0055 Å from the mean plane). The nitro group is twisted 8·9° and the thiocyanate group 6·5° from the mean plane of the backbone.

Introduction. *cis*-3-Nitro-2-thiocyanato-2-butene (I) is one of a series of multiply substituted butenes prepared and investigated by KPP for biological activity. The structure was determined to confirm the stereochemistry and to examine the consequences of the steric crowding. The chemistry of the title compound will be described elsewhere.



(I)

Experimental. Pale-yellow nearly cubic single crystal, 0·40 × 0·41 × 0·42 mm, cut from a large block and wedged in a thin-walled glass capillary because epoxy cement caused decomposition of the crystal. Nicolet *R3m* diffractometer, graphite monochromator, unit-cell parameters by least-squares refinement of 25 reflections ($25 \le 2\theta \le 35°$), θ–2θ scans at variable rates 4·9–29·3° min^{-1}, $2\theta_{\max} = 50°$ for the range $-17 \le h \le 16$, $0 \le k \le 8$, $0 \le l \le 9$, three reflections monitored every 97 reflections with a 4% decrease in intensity over the course of data collection for which a linear correction was applied, 1571 measured intensities, empirical ellipsoidal absorption correction based on ψ scans of six strong reflections (maximum and minimum transmission factors 0·847, 0·898), 1448 unique data (not including space-group absences), $R_{\text{int}} = 0{\cdot}014$, 1171 data with $I > \sigma(I)$ used for refinement. Structure by direct methods, all H atoms found on difference map; for refinement, all C—H bond lengths fixed at 0·96 Å and methyl groups refined as rigid groups with ideal geometry; anisotropic thermal parameters for all non-H atoms and fixed isotropic parameters for H atoms (20% greater than that of carrying C atom). Refined by cascade block-diagonal least squares on F with maximum $(\sin\theta)/\lambda = 0{\cdot}59$ Å^{-1}; refinement of 97 parameters

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converged to $R = 0·040$, $wR = 0·052$; $w = 1/[\sigma^2(F) + 0·0008F^2]$ where $\sigma^2(F)$ is from statistics of counting; goodness of fit = 1·286 (divided by slope of normal probability plot, 1·14); $(\Delta/\sigma)_{\max} = 0·05$ in final cycle; highest peak in final difference map 0·24, lowest hole $-0·15$ e Å^{-3}; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); all calculations were performed on a Data General Eclipse S140 computer using the *SHELXTL* 4·1 program package (Sheldrick, 1984).

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1. Bond lengths and bond angles for non-H atoms are given in Table 2.* (The standard deviations include a 0·0003 fractional error in cell dimensions.) Fig. 1 is a thermal-ellipsoid plot of the molecule showing the atom-numbering scheme. The backbone of the molecule is nearly planar: the mean plane of the six atoms C(1) through C(4), S, N(2) is given by the equation $3·012\,(7)x + 0·664\,(32)y + 6·852\,(36)z = 3·3697\,(54)$ and none of these atoms is more than 0·0055 Å from this plane. The plane of the nitro group O(1)—N(2)—O(2) is tilted 8·9° from the plane of the backbone, with O(1) lying 0·1454 Å below and O(2) 0·1822 Å above in the view of Fig. 1. This distortion appears to be the result of repulsion between the S and O(1) atoms, only 2·468 Å apart (sum of van der Waals radii, 3·25 Å). The thiocyanate group is also twisted slightly out of the plane of the backbone; the torsion angle C(1)—C(2)—S—C(5) is −6·5 (3)° with C(5) and N(1) lying above the plane of the backbone. The thiocyanate group is approximately linear [S—C—N bond angle, 173·3 (3)°]. The dimensions of the butene fragment are near normal values. The bond length C(2)—C(3) = 1·352 Å is slightly longer than expected for a pure double bond; this and the slightly short C(3)—N(2) = 1·443 Å suggest a small contribution from resonance structures involving the nitro group, in spite of its twist of 8·9° out of the plane of the backbone. The contribution of such structures is much less than in a fully conjugated system such as that described by Gate, Meek, Schwalbe, Stevens & Threadgill (1985), where the analogous C—N length is 1·378 Å. The dimensions of the thiocyanate substituent are like those in similar environments; even the 6·7° deviation from linearity is not without precedent (Knuuttila, Knuuttila, Schulze, Mühlstädt & Kaiser, 1982). No unusually short intermolecular contacts appear.

Table 1. *Atom coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2 ×10^3)

Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	6927 (2)	−1423 (3)	2005 (4)	63 (1)
C(2)	7306 (1)	546 (3)	1651 (3)	46 (1)
C(3)	8171 (2)	747 (3)	1254 (3)	49 (1)
C(4)	8858 (2)	−837 (4)	1113 (4)	73 (1)
C(5)	5574 (2)	1430 (3)	2058 (3)	57 (1)
N(1)	4864 (2)	820 (3)	2231 (4)	82 (1)
N(2)	8499 (1)	2679 (3)	915 (3)	55 (1)
O(1)	8036 (1)	4112 (2)	1199 (3)	74 (1)
O(2)	9218 (1)	2838 (3)	325 (3)	81 (1)
S	6576 (1)	2605 (1)	1782 (1)	51 (1)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

C(1)—C(2)	1·496 (3)	C(2)—C(3)	1·352 (3)
C(2)—S	1·772 (2)	C(3)—C(4)	1·486 (3)
C(3)—N(2)	1·443 (3)	C(5)—N(1)	1·138 (3)
C(5)—S	1·704 (3)	N(2)—O(1)	1·230 (3)
N(2)—O(2)	1·219 (3)		
C(1)—C(2)—C(3)	121·4 (2)	C(1)—C(2)—S	117·3 (2)
C(3)—C(2)—S	121·3 (2)	C(2)—C(3)—C(4)	127·1 (2)
C(2)—C(3)—N(2)	119·1 (2)	C(4)—C(3)—N(2)	113·8 (2)
N(1)—C(5)—S	173·3 (2)	C(3)—N(2)—O(1)	119·0 (2)
C(3)—N(2)—O(2)	119·0 (2)	O(1)—N(2)—O(2)	122·0 (2)
C(2)—S—C(5)	99·3 (1)		

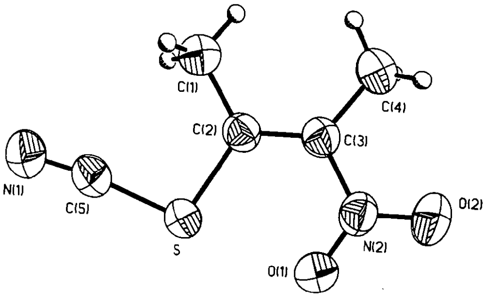

Fig. 1. Molecule of *cis*-3-nitro-2-thiocyanato-2-butene showing the atomic numbering scheme and thermal ellipsoids.

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References

Gate, E. N., Meek, M. A., Schwalbe, C. H., Stevens, M. F. G. & Threadgill, M. D. (1985). *J. Chem. Soc. Perkin Trans.* 2, pp. 251–255.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71, 99, 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Knuuttila, P., Knuuttila, H., Schulze, B., Mühlstädt, M. & Kaiser, J. (1982). *Acta Cryst.* B**38**, 335–337.

Sheldrick, G. M. (1984). *SHELXTL Crystallographic System*, version 4.1. Nicolet XRD Corporation, Madison, Wisconsin.

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* Lists of anisotropic thermal parameters, H-atom parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43582 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.