Acta Cryst. (1978). B**34**, 974–975

4-Dimethylamino-4-*tert*-butyl-1-thiabuta-1,2,3-triene. Evidence for a 1,5-Dipolar Structure

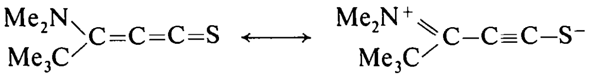
By J. Galloy, J. P. Declercq and M. Van Meerssche

Laboratoire de Chimie Physique et de Cristallographie, Université de Louvain, 1 place Louis Pasteur, B-1348 Louvain-la-Neuve, Belgium

(*Received* 10 *October* 1977; *accepted* 28 *October* 1977)

Abstract. $C_9H_{15}NS$, $M_r = 169{\cdot}3$, monoclinic, space group $P2_1$, $a = 14{\cdot}715$, $b = 7{\cdot}353$, $c = 9{\cdot}532$ Å, $\beta = 100{\cdot}33°$, $V = 1014{\cdot}64$ Å^3, $Z = 4$, $D_x = 1{\cdot}10$ g cm^{-3}, $F(000) = 736$. The structure was refined to an R of 0·075 for 763 counter reflexions. The structure consists of stacks of dipoles oriented alternately and perpendicularly to the 2_1 axes.

Introduction. The synthesis of this heterotriene has led to the concept of cumulogy (Parmantier, Galloy, Van Meerssche & Viehe, 1975). As ^{13}C NMR reveals the participation of the resonance form (II), it was interesting to determine the structural consequences of a π-electron delocalization of this nature.



$$\begin{matrix}Me_2N\\Me_3C\end{matrix}\!\!>C{=}C{=}C{=}S \longleftrightarrow \begin{matrix}Me_2N^+\\Me_3C\end{matrix}\!\!>C{-}C{\equiv}C{-}S^-$$

(I) (II)

The crystals are orange needles of poor quality and oxidize slowly in air. The cell constants were determined from 2θ values of eight reflexions. The systematic absences $0k0$ with $k = 2n + 1$ correspond to space groups $P2_1$ and $P2_1/m$. These two groups are *a priori* equally probable as $Z = 4$. The structure determination shows the correct space group to be $P2_1$ with two molecules in the asymmetric unit. Intensities of 1360 reflexions were measured on a Nonius CAD-4 automatic diffractometer. 763 with $I > 2{\cdot}5\sigma(I)$ were included in the refinement.

The structure was solved with *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). R was 0·075 after refinement by block-diagonal least squares with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).* The weighting scheme was $w = (6{\cdot}82 + |F_o| + 0{\cdot}013|F_o|^2)^{-1}$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). During the refinement, the y coordinate of S was kept fixed. The final coordinates are given in Table 1.

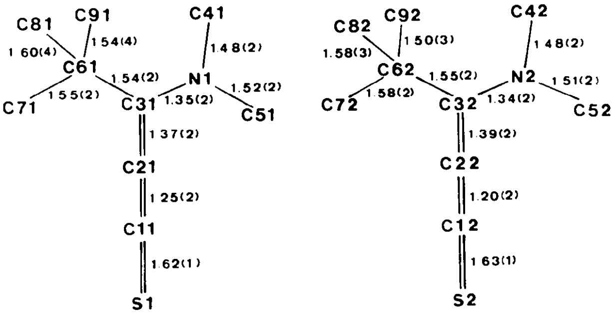


Fig. 1. Bond distances (Å) with standard deviations.

Table 1. *Final coordinates* (×10^4)

	First molecule			Second molecule		
	x	*y*	*z*	*x*	*y*	*z*
C(1)	9092 (8)	8004 (39)	3674 (13)	5683 (9)	3160 (39)	4050 (13)
C(2)	9579 (9)	8211 (42)	4879 (12)	5480 (9)	3217 (45)	5218 (13)
C(3)	9920 (8)	8058 (41)	6310 (12)	5413 (9)	2949 (27)	6642 (13)
C(4)	11372 (10)	8023 (46)	8215 (14)	4316 (10)	3185 (45)	8389 (14)
C(5)	11453 (11)	8020 (61)	5594 (18)	3742 (10)	3257 (51)	5764 (17)
C(6)	9256 (9)	8130 (44)	7390 (13)	6287 (8)	3018 (42)	7822 (14)
C(7)	8247 (9)	8076 (51)	6555 (16)	7148 (9)	2943 (61)	7038 (16)
C(8)	9332 (10)	6182 (32)	8139 (19)	6364 (13)	4797 (34)	8770 (18)
C(9)	9480 (17)	9756 (38)	8417 (20)	6319 (12)	1278 (29)	8645 (20)
N	10849 (7)	8043 (33)	6733 (11)	4568 (7)	3221 (35)	6955 (10)
S	8462 (3)	8182 (0)	2105 (4)	5917 (3)	3133 (15)	2443 (3)

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33128 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

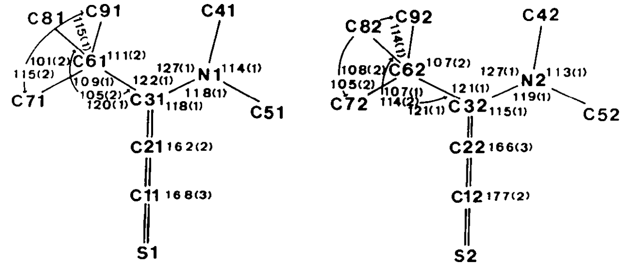


Fig. 2. Angles (°) with standard deviations.

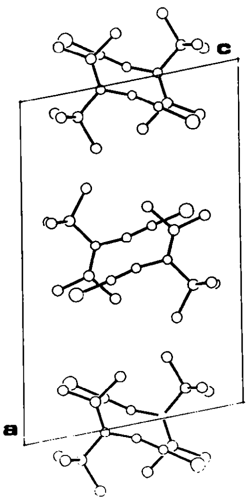


Fig. 3. Title structure viewed along **b**.

Discussion. The interatomic distances and bond angles are given in Figs. 1 and 2.

The distances in the cumulated chain are in agreement with an electronic structure involving an important contribution of the resonance form (II).

C(1)–C(2) (1·23 Å) is much shorter than that observed in a non-conjugated cumulated chain. It is comparable to a triple bond.

C(1)–S is equal to the sum of the covalent radii of a C_{sp} and an S atom.

C(2)–C(3) and C(3)–N indicate conjugation between these bonds. In addition, the cumulated chain and dimethylamino group are coplanar.

The packing of the molecules is shown in Fig. 3.

The authors thank Professor H. G. Viehe for suggesting the problem, M. Parmantier for providing the crystals, and Dr G. Evrard for the data collection. JG and JPD are indebted respectively to the Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture and to the Fonds National Belge de la Recherche Scientifique, for financial assistance.

References

Declercq, J. P., Germain, G., Main, P. & Woolfson, M. M. (1973). *Acta Cryst.* A**29**, 231–234.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Parmantier, M., Galloy, J., Van Meerssche, M. & Viehe, H. G. (1975). *Angew. Chem.* **87**, 33–34.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. & Hall, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1978). B**34**, 975–978

Identification and Structure of 2-Pivaloylmethylene-4-pivaloyldithiolene

By J. Galloy, J.P. Declercq and M. Van Meerssche

Laboratoire de Chimie Physique et de Cristallographie, Université de Louvain, 1 place Louis Pasteur, B-1348 Louvain-la-Neuve, Belgium

(*Received* 10 *October* 1977; *accepted* 28 *October* 1977)

Abstract. $C_{14}H_{20}O_2S_2$, $M_r = 284{\cdot}4$, monoclinic, space group $P2_1/c$, $a = 6{\cdot}080$, $b = 15{\cdot}406$, $c = 9{\cdot}042$ Å, $\beta = 114{\cdot}28°$, $V = 772{\cdot}0$ Å^3, $Z = 2$, $D_x = 1{\cdot}22$ g cm^{-3}, $F(000) = 304$. The structure was refined by rigid-body full-matrix least squares to an R of 0·097 for 1015 counter reflexions. The non-centrosymmetric molecules are situated on inversion centres and are thus disordered.