

- COLAPIETRO, M. & DOMENICANO, A. (1977). *Acta Cryst.* B33, 2240–2243.
- COLAPIETRO, M. & DOMENICANO, A. (1978). *Acta Cryst.* B34, 3277–3280.
- COLAPIETRO, M., DOMENICANO, A. & MARCIANTE, C. (1978). *Ital. Crystallogr. Assoc., 9th Meeting, Sorrento, Italy. Abstr., pp. 75–77.*
- COLAPIETRO, M., DOMENICANO, A. & MARCIANTE, C. (1979). *Acta Cryst.* B35, 2177–2180.
- COLAPIETRO, M., DOMENICANO, A., MARCIANTE, C. & PORTALONE, G. (1979). 5th Eur. Crystallogr. Meeting, Copenhagen, Denmark. *Abstr., p. 288.*
- COLAPIETRO, M., DOMENICANO, A. & PELA CECCARINI, G. (1979). *Acta Cryst.* B35, 890–894.
- DOMENICANO, A., FORESTI SERANTONI, E. & RIVA DI SANSEVERINO, L. (1977). *Acta Cryst.* B33, 1664–1668.
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, 16, 521–523.
- LEISEROWITZ, L. (1976). *Acta Cryst.* B32, 775–802.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, p. 411. London: Macmillan.

Acta Cryst. (1980). B36, 358–363

The Structure of Tetrathiafulvalenium Perchlorate, $\text{TTF}^+ \cdot \text{ClO}_4^-$

BY KYUYA YAKUSHI, SAYURI NISHIMURA, TADASHI SUGANO AND HARUO KURODA

Department of Chemistry, Faculty of Science, University of Tokyo, Hongo, Tokyo 113, Japan

AND ISAO IKEMOTO

Research Centre for Spectrochemistry, Faculty of Science, University of Tokyo, Hongo, Tokyo 113, Japan

(Received 28 June 1979; accepted 13 September 1979)

Abstract

Tetrathiafulvalenium perchlorate ($\text{TTF}^+ \cdot \text{ClO}_4^-$) is orthorhombic, space group *Pbca*, with $a = 16.762$ (1), $b = 20.906$ (2), $c = 12.538$ (1) Å, $Z = 16$. The structure was solved by the direct method and refined by the full-matrix least-squares method to an R of 0.064 for 2324 independent reflections. The TTF^+ ions form dimers, which are arranged in pairs in the crystals. A charge-transfer interaction between TTF^+ ions takes place mostly within a dimer, but a weak interaction is also possible between dimers. The polarized absorption spectrum of a single crystal of $\text{TTF}^+ \cdot \text{ClO}_4^-$ can be interpreted according to the crystal structure.

Introduction

Tetrathiafulvalene (TTF, $\text{C}_6\text{H}_4\text{S}_4$) is an organic molecule of low ionization potential, which forms solid molecular complexes or charge-transfer salts with a variety of electron acceptors. Some TTF complexes exhibit behavior characteristic of one-dimensional metals. The solid complex with tetracyano-*p*-quinodimethane (TCNQ) is a typical example of such an organic metal. $\text{TTF} \cdot \text{Br}_{0.7}$ and $\text{TTF} \cdot \text{I}_{0.76}$ are also known to exhibit metallic behavior at room temperature. All these highly conductive TTF complexes have one-dimensional TTF stacks in their crystal

structures, which have mixed valences, *i.e.* the TTF molecules are partially in the state of a monocationic ion (TTF^+) and partially in the state of a neutral molecule (TTF^0). In our previous study on the absorption spectra of the crystals of TTF halides and related salts, we found that the spectrum of $\text{TTF}^+ \cdot \text{ClO}_4^-$ shows several features distinctly different from those of the spectra of the mixed-valence TTF halides (Sugano, Yakushi & Kuroda, 1978). Thus it becomes necessary to determine the crystal structure to interpret the observed spectrum. It is also of interest to know the geometry of the TTF^+ ion. Although the TTF geometries in several mixed-valence TTF salts have been reported, the geometry of the TTF^+ ion in crystals where TTF molecules are entirely in the form of monocationic ions has not been reported so far. Since $\text{TTF}^+ \cdot \text{ClO}_4^-$ is completely ionic, the analysis of its crystal structure can provide data concerned with the molecular geometry of the TTF^+ ion.

Experimental

$\text{TTF}^+ \cdot \text{ClO}_4^-$ was prepared according to the method reported by Wudl (1975). The dark-purple crystals of $\text{TTF}^+ \cdot \text{ClO}_4^-$ were grown by slowly cooling a solution in acetonitrile; they were elongated along a , developing the (001) crystal face. From Weissenberg photographs the space group was determined to be *Pbca*, since the

following systematic absences of reflections were observed: $0kl$ when $k = 2n + 1$, $h0l$ when $l = 2n + 1$ and $hk0$ when $h = 2n + 1$. The lattice parameters and the intensity data were obtained with a Rigaku four-circle automatic diffractometer employing Mo $K\alpha$ radiation monochromatized with graphite. The dimensions of the single crystal used for the intensity collection were $0.5 \times 0.3 \times 0.05$ mm.

Crystal data

$a = 16.762$ (1), $b = 20.906$ (2), $c = 12.538$ (1) Å, $V = 4393.6$ (8) Å³. Formula: $C_6H_4S_4^+ \cdot ClO_4^-$, FW = 303.8, $D_c = 1.84$, $D_m = 1.82$ Mg m⁻³ (by flotation), $Z = 16$, $\mu = 0.278$ mm⁻¹ (Mo $K\alpha$).

Table 1. Fractional coordinates and their standard deviations

	<i>x</i>	<i>y</i>	<i>z</i>
TTF ⁺ (1)			
S(1)	0.0062 (2)	0.1076 (1)	0.1432 (2)
S(2)	0.1715 (2)	0.1140 (1)	0.0769 (2)
S(3)	0.0131 (1)	-0.0449 (1)	0.1448 (2)
S(4)	0.1794 (1)	-0.0420 (1)	0.0806 (2)
C(1)	0.0460 (9)	0.1824 (6)	0.1185 (8)
C(2)	0.1199 (8)	0.1860 (5)	0.0903 (8)
C(3)	0.0611 (7)	-0.1168 (5)	0.1261 (8)
C(4)	0.1361 (6)	-0.1164 (5)	0.0982 (7)
C(12)	0.0913 (5)	0.0676 (5)	0.1093 (7)
C(34)	0.0946 (5)	0.0003 (5)	0.1089 (6)
H(1)	0.011 (6)	0.211 (4)	0.124 (8)
H(2)	0.156 (5)	0.216 (4)	0.079 (6)
H(3)	0.032 (5)	-0.148 (4)	0.139 (6)
H(4)	0.171 (4)	-0.147 (3)	0.080 (6)
TTF ⁺ (2)			
S(5)	0.0755 (2)	0.1230 (1)	0.3939 (2)
S(6)	0.2414 (2)	0.1189 (1)	0.3298 (2)
S(7)	0.0730 (2)	-0.0325 (1)	0.4034 (2)
S(8)	0.2379 (1)	-0.0350 (1)	0.3356 (2)
C(5)	0.1228 (8)	0.1952 (6)	0.3702 (8)
C(6)	0.1988 (8)	0.1936 (6)	0.3429 (9)
C(7)	0.1181 (8)	-0.1054 (6)	0.3903 (8)
C(8)	0.1924 (7)	-0.1069 (5)	0.3586 (8)
C(56)	0.1583 (5)	0.0773 (5)	0.3661 (6)
C(78)	0.1571 (5)	0.0104 (5)	0.3696 (6)
H(5)	0.088 (6)	0.225 (5)	0.387 (8)
H(6)	0.233 (7)	0.222 (5)	0.332 (9)
H(7)	0.082 (5)	-0.131 (4)	0.394 (7)
H(8)	0.220 (5)	-0.140 (4)	0.351 (7)
ClO ₄ ⁻ (1)			
Cl(1)	0.1218 (1)	0.3640 (1)	0.1857 (2)
O(1)	0.1882 (5)	0.3338 (4)	0.1393 (8)
O(2)	0.0512 (4)	0.3326 (4)	0.1546 (6)
O(3)	0.1191 (6)	0.4284 (4)	0.1507 (7)
O(4)	0.1273 (5)	0.3640 (4)	0.2988 (6)
ClO ₄ ⁻ (2)			
Cl(2)	0.3763 (2)	0.2040 (1)	0.1368 (2)
O(5)	0.4445 (5)	0.2263 (4)	0.0840 (9)
O(6)	0.3065 (5)	0.2208 (4)	0.0807 (9)
O(7)	0.3794 (6)	0.1363 (4)	0.1419 (8)
O(8)	0.3737 (7)	0.2302 (6)	0.2380 (9)

We obtained 2324 independent reflections with $|F_o| > 3\sigma(F_o)$ by measuring all reflections with $2\theta < 55^\circ$. No corrections were applied for absorption or extinction.

Structure determination and refinement

The structure was solved by the direct method using the program *DP35* written by S. R. Hall. Among 594 reflections with $E \geq 1.00$, 12,6,1, 317 and 10,9,6 were chosen to determine the origin. To obtain an E map, it was necessary to assume the signs of three other reflections. We chose the reflections, 772, 213 and 7,14,2 for this purpose, and obtained E maps corresponding to all possible combinations of the assumed signs. Among the eight ($= 2^3$) E maps, we found one that clearly showed the Cl and S atoms at reasonable positions. All the remaining atoms appeared in a Fourier map computed using the positions of S and Cl atoms. At this stage R was 0.28. The parameters were refined by the block-diagonal least-squares method, and subsequently by the full-matrix least-squares method, including the anomalous-dispersion terms of the atomic scattering factors of the S and Cl atoms. The final R value was 0.064. The value of $[\sum w(|F_o| - |F_c|)^2 / (n - m)]^{1/2}$ with the weighting scheme $w = [\sigma^2(F_o) + (0.06F_o)^2]^{-1}$, where n and m are respectively the numbers of reflections and parameters. Atomic scattering factors for C, O, S and Cl were taken from *International Tables for X-ray Crystallography* (1974), and those for H were from Stewart, Davidson & Simpson (1965).

Results and discussion

Arrangement of molecules

Atomic coordinates are given in Table 1.* A projection of the crystal structure along the c axis is illustrated in Fig. 1. The molecules drawn with broken lines lie at positions $c/2$ above those drawn with solid lines. As shown in this figure, the long axis of the TTF molecule is almost parallel to the b axis. The arrangement of the TTF molecules projected along the b axis is schematically drawn in Fig. 2. The crystal structure is composed of TTF cation dimers and perchlorate anions; the unit cell contains eight TTF cation dimers. The charge-transfer interaction is likely to take place mostly within the dimer, but an interaction is also

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34824 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

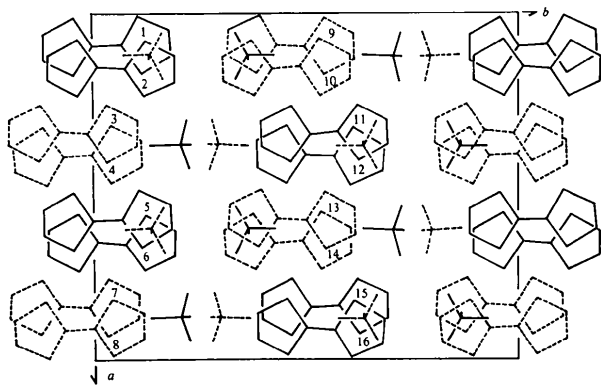


Fig. 1. A projection of the molecular arrangement along the c axis. The molecules drawn with broken lines lie at positions $c/2$ above those drawn with solid lines.

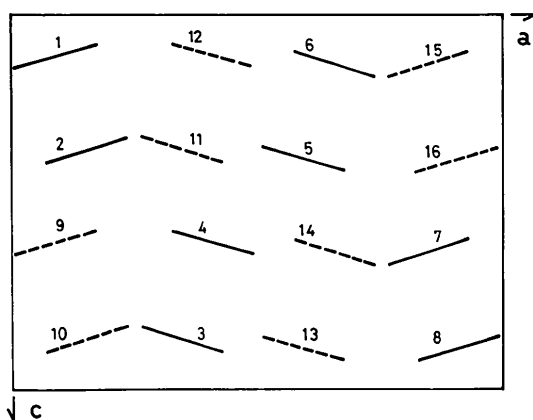


Fig. 2. A schematic drawing of TTF molecules projected along the b axis. The molecules drawn with broken lines lie at positions $b/2$ above those drawn with solid lines.

possible between TTF cations belonging to neighboring dimers, for example between molecules 4 and 5, which are related to each other by a center of symmetry. In this sense, we could consider molecules 3, 4, 5 and 6 to form a tetrameric group, and the unit cell to contain four of these tetrameric groups which are crystallographically equivalent to each other.

The molecular overlap in the TTF dimer is shown in Fig. 3(a). The average intermolecular separation in the dimer is 3.41 Å and the dihedral angle between the molecular planes is 0.4°. The intermolecular distances between S atoms are significantly shorter than the sum of the van der Waals radii (3.70 Å): 3.555 (3) for S(1)–S(5), 3.382 (4) for S(2)–S(6), 3.405 (3) for S(3)–S(7) and 3.347 (3) Å for S(4)–S(8). The geometry of the dimer is almost the same as that in the TTF–Br crystal (Scott, La Placa, Torrance, Silverman & Welber, 1977), where the intermolecular separation in the dimer is 3.35 Å. The intermolecular separation mentioned above is much shorter than those of the

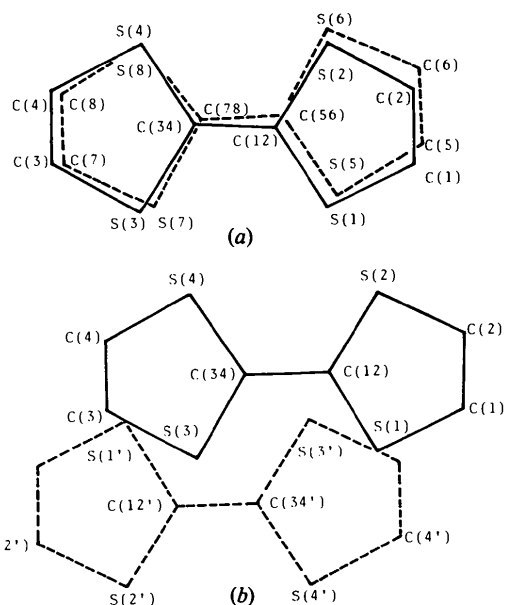


Fig. 3. (a) Molecular overlap in a TTF dimer, e.g. molecules 3 and 4. (b) Molecular overlap between TTF dimers, e.g. molecules 4 and 5.

highly conductive TTF halides: 3.57 Å for TTF–Br_{0.76} (Scott *et al.*, 1977), 3.56 Å for TTF–I_{0.71} (Johnson & Watson, 1976), 3.61–3.63 Å for TTF–SCN_{0.55–0.58} (Kobayashi & Kobayashi, 1977; Somoano *et al.*, 1977; Wudl *et al.*, 1977). In these highly conductive crystals, TTF molecules are uniformly stacked although the overlap between the neighboring TTF molecules is almost the same as that in the TTF dimer of TTF⁺.ClO₄[–]. The overlap between dimers (e.g. molecules 4 and 5) in TTF⁺.ClO₄[–] is shown in Fig. 3(b). The shortest interatomic distance between molecules 4 and 5 is 3.564 (10) Å for S(1)–C(3'), and the average intermolecular separation is 3.54 Å. These results suggest that the charge-transfer interaction between dimers must be considerably weaker than those within the dimer.

Another distance significantly shorter than a van der Waals contact is that between an S atom of the TTF cation and an O atom of the perchlorate anion. It appears that there is a relatively strong interaction between these atoms.

Molecular geometry

The TTF⁺ ion is almost planar. The equations of the least-squares planes of the two TTF⁺ ions [TTF⁺(1) and TTF⁺(2)] in the TTF⁺.ClO₄[–] crystal are given in Table 2, together with the deviations of atoms from the planes. The molecular geometries of TTF⁺(1) and TTF⁺(2) are shown in Fig. 4. There is no significant and/or systematic difference between the determined geometries of TTF⁺(1) and TTF⁺(2). In both cases, the

Table 4. Bond lengths (Å) and bond angles (°) in the ClO_4^- groups with their standard deviations

ClO_4^- (1)		ClO_4^- (2)	
Cl(1)—O(1)	1.406 (9)	Cl(2)—O(5)	1.401 (9)
Cl(1)—O(2)	1.408 (7)	Cl(2)—O(6)	1.409 (10)
Cl(1)—O(3)	1.416 (9)	Cl(2)—O(7)	1.419 (8)
Cl(1)—O(4)	1.422 (8)	Cl(2)—O(8)	1.382 (12)
O(1)—Cl(1)—O(2)	110.0 (5)	O(5)—Cl(2)—O(6)	111.0 (6)
O(1)—Cl(1)—O(3)	108.9 (5)	O(5)—Cl(2)—O(7)	108.8 (5)
O(1)—Cl(1)—O(4)	111.1 (5)	O(5)—Cl(2)—O(8)	109.1 (7)
O(2)—Cl(1)—O(3)	109.3 (5)	O(6)—Cl(2)—O(7)	107.6 (5)
O(2)—Cl(1)—O(4)	109.4 (5)	O(6)—Cl(2)—O(8)	109.4 (7)
O(3)—Cl(1)—O(4)	108.2 (5)	O(7)—Cl(2)—O(8)	110.8 (7)

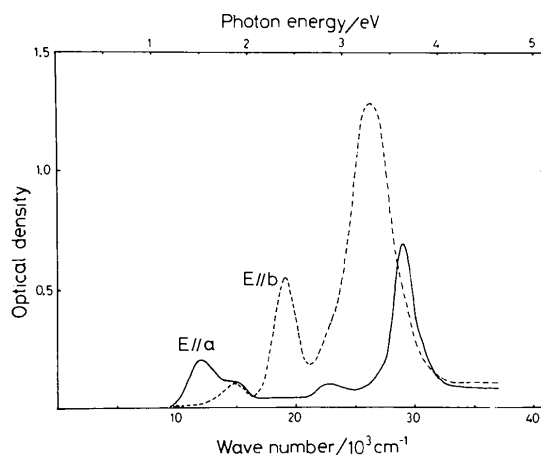


Fig. 5. Polarized absorption spectra on the (001) crystal face of the $\text{TTF}^+ \cdot \text{ClO}_4^-$ single crystal (Sugano, Yakushi & Kuroda, 1978).

Comparison with the absorption spectrum

The absorption spectra of $\text{TTF}^+ \cdot \text{ClO}_4^-$, observed on the (001) plane of the single crystal for light polarized parallel to the a axis and for that polarized parallel to the b axis, were reported in our previous paper (Sugano, Yakushi & Kuroda, 1978). The observed spectra are reproduced in Fig. 5. The absorption bands in the region of 16×10^3 – $33 \times 10^3 \text{ cm}^{-1}$ are those associated with the intramolecular transitions of TTF^+ . According to the crystal structure determined in the present study, the absorption bands due to the long-axis polarized transitions of TTF^+ should appear in the $\parallel b$ spectrum, while those due to the short-axis polarized transitions should appear in the $\parallel a$ spectrum, and their intensities are expected to be approximately proportional to the intensities of the corresponding absorption bands in the solution spectrum of TTF^+ . This is in good agreement with the results found in our previous study.

The absorption bands in the region 10×10^3 – $16 \times 10^3 \text{ cm}^{-1}$ are due to charge transfer between TTF^+ ions. In our previous paper, we were not able to explain the origin of these two charge-transfer (CT) bands

because the crystal structure was not known at that time. Now we know that there are two types of TTF overlap in the $\text{TTF}^+ \cdot \text{ClO}_4^-$ crystal, *i.e.* the intradimer overlap and the interdimer overlap (see Fig. 3). The overlap integral between the half-filled molecular orbitals of two TTF^+ ions must be appreciably larger within a dimer than between dimers. Thus, we can expect that the oscillator strength of the intradimer CT transition will be significantly larger than that of the interdimer CT transition. We can also expect that the energy of the intradimer CT transition will be lower than that of the interdimer CT transition because of the larger contribution of the Coulomb energy term. If we assume that the transition moment is in the direction connecting the centers of the TTF ions concerned with the charge transfer, the polarization ratio I_b/I_a is expected to be 0.04 for the intradimer CT transition, and 0.2 for the interdimer CT transition. Thus the former will appear almost exclusively in the $\parallel a$ spectrum, while the latter can appear not only in the $\parallel a$ spectrum but also in the $\parallel b$ spectrum. All these considerations suggest that the lower-energy CT band at $12 \times 10^3 \text{ cm}^{-1}$ is due to the intradimer CT transition and that at $15 \times 10^3 \text{ cm}^{-1}$ is due to the interdimer CT transition.

The computer used was a HITAC 8700/8800 at the Computer Center, University of Tokyo, with the UNICS (1967) system of programs.

References

- COMES, R., SHIRANE, G., SHAPIRO, S. M., GARITO, A. F. & HEEGER, A. J. (1976). *Phys. Rev. B*, **14**, 2376–2383.
- COOPER, W. F., KENNY, N. C., EDMONDS, J. W., NAGEL, A., WUDL, F. & COPPENS, P. (1971). *Chem. Commun.* pp. 889–890.
- IKEMOTO, I., SUGANO, T. & KURODA, H. (1977). *Chem. Phys. Lett.* **49**, 45–48.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. & WATSON, C. R. JR (1976). *J. Chem. Phys.* **64**, 2271–2286.
- KAGOSHIMA, S., ISHIGURO, T. & ANZAI, H. (1976). *J. Phys. Soc. Jpn.* **41**, 2061–2071.
- KISTENMACHER, T. J., PHILLIPS, T. E. & COWAN, D. O. (1974). *Acta Cryst.* **B30**, 763–768.
- KOBAYASHI, H. & KOBAYASHI, K. (1977). *Bull. Chem. Soc. Jpn.* **50**, 3127–3130.
- SCHULTZ, A. J., STUCKY, G. D., CRAVEN, R., SCHAFFMAN, M. J. & SALAMON, M. B. (1976). *J. Am. Chem. Soc.* **98**, 5191–5197.
- SCOTT, B. A., LAPLACA, S. J., TORRANCE, J. B., SILVERMAN, B. D. & WELBER, B. (1977). *J. Am. Chem. Soc.* **99**, 6631–6639.
- SOMOANO, R. B., GUPTA, A., HADEK, V., NOVOTNY, M., JONES, M., DATTA, T., DECK, R. & HERMAN, A. M. (1977). *Phys. Rev. B*, **15**, 595–601.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

SUGANO, T., YAKUSHI, K. & KURODA, H. (1978). *Bull. Chem. Soc. Jpn.* **51**, 1041–1046.
 UNICS (1967). *The Universal Crystallographic Computation Program System*, edited by T. SAKURAI. The Crystallographic Society of Japan.
 WUDL, F. (1975). *J. Am. Chem. Soc.* **97**, 1962–1963.

WUDL, F., SCHAFER, D. E., WALSH, W. M. JR, RUPP, L. W., DiSALVO, F. J., WASZCZAK, J. V., KAPLAN, M. L. & THOMAS, G. A. (1977). *J. Chem. Phys.* **66**, 377–385.
 ZAHRADNIK, R., CARSKY, P., HUNIG, S., KIESSLICH, G. & SCHEUTZOW, D. (1971). *Int. J. Sulfur Chem. Part C*, **6**, 109–122.

Acta Cryst. (1980). **B36**, 363–368

The Structures of 2-(2,6-Dichlorophenyl)imino-3-methylperhydro-1,3-thiazine, 2-(2,6-Dimethylphenyl)imino-3-methylperhydro-1,3-thiazine and 2-[N-(2,6-Dimethylphenyl)-N-methylamino]-4,5-dihydro-6H-1,3-thiazine

BY GYULA ARGAY AND ALAJOS KÁLMÁN

Central Research Institute of Chemistry, Hungarian Academy of Sciences, Budapest, POB 17, H-1525, Hungary

AND ÁGNES KAPOR AND BÉLA RIBÁR

Institute of Physics, Faculty of Sciences, Ilije Djuricica 4, 21000 Novi Sad, Yugoslavia

(Received 15 June 1979; accepted 18 September 1979)

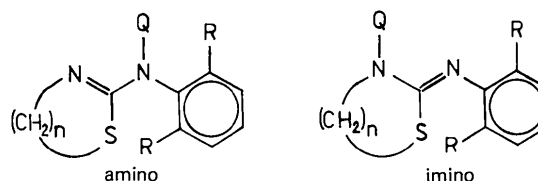
Abstract

The structures of the title compounds have been established by X-ray crystallography from diffractometer data. Crystals of the first, $C_{11}H_{12}Cl_2N_2S$ (III), are monoclinic, space group $P2_1/c$, with $a = 12.741$ (6), $b = 9.636$ (5), $c = 20.432$ (8) Å, $\beta = 96.36$ (4)°, $Z = 8$. Crystals of the second, $C_{13}H_{18}N_2S$ (IV), are orthorhombic, space group $Pna2_1$, with $a = 15.169$ (7), $b = 9.775$ (3), $c = 8.801$ (3) Å, $Z = 4$. Crystals of the third, $C_{13}H_{18}N_2S$ (V), are monoclinic, space group $P2_1/c$, with $a = 12.118$ (8), $b = 7.709$ (7), $c = 14.658$ (11) Å, $\beta = 105.76$ (9)°, $Z = 4$. The structures were refined to $R = 0.051$ for 2919 reflexions of (III), $R = 0.063$ for 1261 reflexions of (IV) and $R = 0.095$ for 1405 reflexions of (V). The characteristic features of the geometries (amino or imino form) of the cyclic amidine (thiourea) groups in 2-arylamino-1,3-thiazines and their dependence on the position of substituent (H, alkyl, acyl) are shown and discussed. The mean $S^{II}-C(sp^3)$ and $S^{II}-C(sp^2)$ lengths [1.803 (5) and 1.766 (3) Å] for the title compounds and other structures discussed indicate single bonds and agree well with expected values.

Introduction

In the course of a systematic X-ray analysis of various 2-arylamino(imino)thiazoli(d)ines ($n = 2$) (Argay,

Kálmán, Lazar, Ribár & Tóth, 1977; Kálmán & Argay, 1978*b*, and references therein) and analogous 1,3-thiazines ($n = 3$),



the structures of 2-phenyliminoperhydro-1,3-thiazine (I) and 2-(2,6-dimethylphenyl)iminoperhydro-1,3-thiazine (II) (Kálmán, Argay, Ribár & Toldy, 1977; Argay, Kálmán, Kapor & Ribár, 1977) together with two derivatives of (II) with $Q =$ methylsulphonyl [hereinafter (VI) for the *endo* and (VII) for the *exo* substituent] have been published (Kálmán & Argay, 1978*a*; Kálmán, Argay & Vassányi, 1977). Now we report the structures of three methyl derivatives ($n = 3$, $Q =$ Me) termed as (III), (IV) and (V). The differences among these three structures [(III): $R =$ Cl, Q *endo*; (IV): $R =$ Me, Q *endo*; (V): $R =$ Me, Q *exo*] allow the study of their effects upon the electronic structures (geometries) of the amidine groups. They allow us also to corroborate our conclusions that the predominant tautomeric form ($Q =$ H *endo*) of (I) and (II) and their thiazolidine analogues (Petrović, Ribár, Argay, Kálmán & Nowacki, 1977; Argay, Kálmán, Lazar, Ribár & Tóth, 1977) could be distinguished unambiguously on the basis of five inequalities observed for the bond lengths