(2*b*) with respect to $[N(C_2H_5)_4]^+$ in (1*a*) and $[PPh_4]^+$ in (2*a*), these latter cations establishing nonequivalent sets of electrostatic and van der Waals interactions with the respective anions. Unfortunately, beside the recognition of the different interactions between the anions and the surrounding cations, there is no simple rationalization of the causes of the observed shrinkage of one triangular face with respect to the other in (1*a*) and (2*a*). Nonetheless, these observations strengthen the idea that the inner metal-atom polyhedra have to be regarded as the 'soft' cores of these species, capable of adapting themselves to the steric and electronic demands of both the ligands packed around the core and the surrounding molecules.

Concluding remarks

We have shown that there is a clear borderline between the knowledge of the structural parameters concerning the ligands and those related to the metal cores in transition-metal clusters. *M*–*M* bonds and angles can be determined with great precision, but appear to be related to relatively adaptable parts of the molecules, which can be easily affected by small changes in both ligand coverages and crystal packing. On the other hand, the parameters related to metal–ligand (or ligand–ligand) interactions and which contain more 'chemical information', are known with reduced precision and are significantly dependent on experimental limitations and refinement strategies.

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References

ALBANO, V. G., BRAGA, D., GREPIONI, F., DELLA PERGOLA, R., GARLASCHELLI, L. & FUMAGALLI, A. (1988). *J. Chem. Soc. Dalton Trans.* In the press.
ALBANO, V. G., BRAGA, D. & MARTINENGO, S. (1981). *J. Chem. Soc. Dalton Trans.* pp. 717–720.
ALBANO, V. G., BRAGA, D. & MARTINENGO, S. (1986). *J. Chem. Soc. Dalton Trans.* pp. 981–984.
ALBANO, V. G., CHINI, P. & SCATTURIN, V. (1968). *J. Organomet. Chem.* **15**, 423–432.
ALBANO, V. G., SANSONI, M., CHINI, P. & MARTINENGO, S. (1973). *J. Chem. Soc. Dalton Trans.* pp. 651–655.
BAR, I. & BERNSTEIN, J. (1984). *J. Phys. Chem.* **88**, 243–248.
BERNSTEIN, J. & HAGLER, A. T. (1978). *J. Am. Chem. Soc.* **100**, 673–681.
BRAGA, D. & GREPIONI, F. (1987). *J. Organomet. Chem.* **336**, C9–C12.
BRAGA, D. & KOETZLE, T. F. (1987). *J. Chem. Soc. Chem. Commun.* pp. 144–146.
BRAGA, D. & KOETZLE, T. F. (1988). *Acta Cryst.* B**44**, 151–155.
CARRE', F. H., COTTON, F. A. & FRENZ, B. A. (1976). *Inorg. Chem.* **15**, 380–387.
COLTON, R. & MCCORMICK, M. J. (1980). *Coord. Chem. Rev.* **31**, 1–52.
CONNOR, J. A. (1980). *Transition Metal Clusters*, edited by B. F. G. JOHNSON, pp. 345–389. New York: John Wiley.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
JOHNSON, B. F. G. & BENFIELD, R. E. (1981). *Inorg. Organomet. Stereochem.* **12**, 253–335, and references therein.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
LAUHER, J. W. (1986). *J. Am. Chem. Soc.* **108**, 1521–1531.
MARTINENGO, S., STRUMOLO, D., CHINI, P., ALBANO, V. G. & BRAGA, D. (1985). *J. Chem. Soc. Dalton Trans.* pp. 35–41.
SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
WALKER, N. & STUART, D. (1983). *Acta Cryst.* A**39**, 158–166.
WEI, C. H. (1966). *Inorg. Chem.* **8**, 2384–2397.

Acta Cryst. (1989). B**45**, 65–69

Deformation Density Studies of Tetramethylthiuram Disulfide and Tetraethylthiuram Disulfide

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Abstract

Two thiuram disulfide compounds, whose room-temperature structures have been reported previously, were studied by X-ray diffraction at low temperature. Tetramethylthiuram disulfide (1), $C_6H_{12}N_2S_4$, $M_r = 240{\cdot}4$, monoclinic, $C2/c$, $a = 9{\cdot}524$ (4), $b = 9{\cdot}911$ (3), $c = 11{\cdot}795$ (1) Å, $\beta = 99{\cdot}22$ (1)°, $V = 1099$ Å^3, $Z = 4$, $D_x = 1{\cdot}47$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 7{\cdot}7$ cm^{-1}, $T = 138$ K, final $R = 0{\cdot}031$ for 2881 reflections. Tetraethylthiuram disulfide (2), $C_{10}H_{20}N_2S_4$, $M_r = 296{\cdot}5$, monoclinic, $P2_1/c$, $a = 10{\cdot}922$ (3), $b =$

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15·946 (4), $c = 8·444$ (1) Å, $\beta = 91·92$ (1)°, $V = 1469·8$ (8) Å^3, $Z = 4$, $D_x = 1·34$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 6·0$ cm^{-1}, $T = 105$ K, final $R = 0·029$ for 5772 reflections. Both compounds contain a disulfide bridge connecting two identical thiuram moieties. The S—S bonds, with lengths 2·0041 (6) and 2·0057 (6) Å for (1) and (2) respectively, are essentially single bonds. The tetramethyl derivative undergoes a phase transition at 133 K, the high-temperature molecular structure has C_2 symmetry. There are C=S double and C—S single bonds in both molecules. The accumulations of electron density along the C—N and C—S bonds in the experimental deformation density maps are as expected. The lone pair around S is also observed. The unusual deformation density along the S—S bond is comparable with other recent work on compounds containing S—S bonds; it can be reasonably explained by theoretical density calculations.

Introduction

Tetramethylthiuram disulfide (1) was considered to be an ideal system for a deformation density study for the following reasons: first, the molecule contains various C—N, C—S, S—S bonds; second, the molecular symmetry is C_2, and the total number of parameters is small; therefore, the accuracy of the atomic parameters will be improved. Unfortunately, there is a phase transition below 133 K, and the low-temperature phase can not be easily determined. Although a set of data was collected at 138 K, and a deformation density study was made, the results were not as good as we would wish. In order to obtain better results, tetraethylthiuram disulfide (2) was studied at 105 K. There is no C_2 symmetry in the molecule; however, the two halves of the molecule are chemically equivalent. The room-temperature structures of both compounds have been investigated previously (Wang, Liao & Ueng, 1986; Karle, Estlin & Britts, 1967).

Experimental

The title compounds were synthesized according to the literature (Cummings & Simmons, 1928). Suitable light-yellow crystals were obtained by slow evaporation from $C_2H_5OH/CHCl_3$ solution. The crystal data and some details of the experimental conditions are given in Table 1. Low-temperature data were measured on a CAD-4 diffractometer equipped with a liquid N_2 gas-flow set up. Unique sets of reflections were measured up to $\theta = 42$, 36° for compounds (1) and (2) respectively. Seven measurements of ψ values from −45 to 45° with a step of 15° were also collected for each reflection up to $\theta = 20$ and 16° for (1) and (2) respectively; beyond these angles, only one additional measurement with $\psi = 15°$ was collected. The standard deviation of the intensity is defined as $\sigma^2(I) = \sigma_c^2(I) + (fI_{net})^2$, where f is 0·01 and 0·02 for (1) and (2) respectively, and $\sigma^2(F_o)$ values are calculated accordingly. Normal least-squares refinements were performed; the final agreement indices are given in Table 1. Additional high-order refinements were carried out on data with $\sin\theta/\lambda > 0·75$, $> 0·65$ Å^{-1} for (1) and (2) respectively, in order to obtain all the non-H atomic parameters for use in promolecule model density calculations. The deformation density distributions were all calculated up to maximum $\sin\theta/\lambda$ of 0·75 Å^{-1}.

Table 1. *Crystal data of compound* (1) *at* 138 K *and of compound* (2) *at* 105 K

	(1)	(2)
Space group	$C2/c$	$P2_1/c$
a (Å)	9·524 (4)	10·922 (3)
b (Å)	9·911 (3)	15·956 (4)
c (Å)	11·795 (1)	8·444 (1)
β (°)	99·22 (1)	91·92 (1)
θ range (°) for cell-parameter determination	11–35	10–30
V (Å^3)	1099 (2)	1469·8 (8)
D_x (g cm^{-3})	1·47	1·34
Z	4	4
T (K)	138	105
Crystal size (mm)	0·40 × 0·47 × 0·47	0·26 × 0·35 × 0·52
λ(Mo $K\alpha$) (Å)	0·7107	0·7107
μ (cm^{-1})	7·7	6·0
Transmission range	0·73–0·83	0·82–0·87
θ_{max} (°)	42	36
No. of measurements	19 016	29 759
No. of unique reflections	3355	6861
R_{int}	0·021	0·016
No. of observed reflections	2881 (>4σ), 1085*	5772 (>2·5σ), 2704*
No. of parameters	79, 55*	226, 145*
R	0·031, 0·032*	0·029, 0·024*
wR	0·040, 0·031*	0·023, 0·023*
S	4·32, 1·34*	5·55, 1·69*
hkl range	−17→16 0→18 0→21	−19→19 0→27 0→14
$(\Delta/\sigma)_{max}$	0·16	0·06
$\Delta\rho_{max}$ (e Å^{-3})	0·44	0·58

* High-order refinement: $\sin\theta/\lambda > 0·75$ Å^{-1} for (1), $> 0·65$ Å^{-1} for (2).

Results

Atomic fractional coordinates of (1) and (2) are given in Tables 2 and 3* respectively. The coordinates include one set (top line) from the full data refinements and one set (bottom line) from the high-order refinements. The bond lengths and the atomic numbering schemes are given in Fig. 1. The corresponding distances for both compounds at room temperature are essentially the same (Wang, Liao & Ueng, 1986). At low temperature, however, the differences are more than those at room temperature, although it has to be remembered that the two compounds were studied at slightly different temperatures. S—S bonds are the same within standard deviations. The C=S bond is shorter in

* Lists of anisotropic temperature factors of non-H atoms, positional and isotropic thermal parameters of H atoms, and structure factors for both compounds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51264 (67 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic fractional coordinates and equivalent isotropic thermal parameters of compound* (1)

a Full data refinement at 138 K, *b* high-order refinement at 138 K ($\sin\theta/\lambda > 0.75$ Å^{-1}).

$$B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

		x	y	z	B_{eq}(Å^2)
S(1)	*a*	0·19841 (2)	0·39273 (2)	0·20381 (2)	2·212 (8)
	b	0·19839 (3)	0·39286 (3)	0·20370 (3)	2·14 (1)
S(2)	*a*	−0·02877 (3)	0·17177 (3)	0·16448 (3)	2·66 (1)
	b	−0·02884 (4)	0·17170 (4)	0·16431 (4)	2·58 (1)
N(1)	*a*	0·06138 (9)	0·31165 (9)	0·00115 (8)	2·22 (3)
	b	0·0615 (1)	0·3115 (1)	0·00078 (9)	2·14 (2)
C(1)	*a*	0·08331 (9)	0·30095 (9)	0·11476 (9)	1·79 (3)
	b	0·08358 (9)	0·30111 (8)	0·11519 (8)	1·72 (2)
C(2)	*a*	0·1403 (2)	0·4084 (1)	−0·0573 (1)	2·99 (4)
	b	0·1408 (2)	0·4091 (2)	−0·0577 (2)	2·86 (4)
C(3)	*a*	−0·0426 (1)	0·2315 (2)	−0·0763 (1)	3·47 (5)
	b	−0·0430 (2)	0·2330 (3)	−0·0769 (2)	3·34 (5)

Table 3. *Atomic fractional coordinates and equivalent isotropic thermal parameters of compound* (2)

a Full data refinement at 105 K, *b* high-order data refinement at 105 K ($\sin\theta/\lambda > 0.65$ Å^{-1}).

$$B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

		x	y	z	B_{eq}(Å^2)
S(1)	*a*	0·33884 (3)	0·32932 (2)	0·21376 (4)	1·58 (1)
	b	0·33902 (2)	0·32931 (2)	0·21369 (4)	1·461 (9)
S(2)	*a*	0·17114 (2)	0·45455 (2)	0·04118 (3)	1·177 (9)
	b	0·17121 (2)	0·45458 (1)	0·04104 (3)	1·070 (6)
S(3)	*a*	0·32816 (2)	0·51772 (2)	0·07946 (3)	1·170 (9)
	b	0·32812 (2)	0·51775 (1)	0·07935 (3)	1·060 (6)
S(4)	*a*	0·16524 (3)	0·57668 (2)	0·34445 (3)	1·64 (1)
	b	0·16509 (2)	0·57670 (2)	0·34438 (4)	1·519 (8)
N(1)	*a*	0·10024 (7)	0·30753 (5)	0·14742 (9)	0·96 (3)
	b	0·10008 (7)	0·30736 (5)	0·14707 (9)	0·98 (2)
N(2)	*a*	0·40204 (8)	0·61391 (5)	0·3175 (1)	1·05 (3)
	b	0·40232 (7)	0·61394 (5)	0·3179 (1)	1·08 (2)
C(1)	*a*	0·13508 (1)	0·15661 (8)	0·0935 (2)	1·48 (5)
	b	0·13503 (9)	0·15642 (6)	0·0930 (1)	1·42 (2)
C(2)	*a*	0·1057 (1)	0·22223 (7)	0·2160 (1)	1·20 (4)
	b	0·10587 (8)	0·22234 (6)	0·2162 (1)	1·20 (2)
C(3)	*a*	−0·0230 (1)	0·33579 (7)	0·0936 (1)	1·13 (4)
	b	−0·02314 (7)	0·33544 (6)	0·0929 (1)	1·09 (2)
C(4)	*a*	−0·0916 (1)	0·37720 (8)	0·2257 (2)	1·46 (5)
	b	−0·09174 (9)	0·37724 (7)	0·2261 (1)	1·40 (2)
C(5)	*a*	0·20087 (9)	0·35518 (6)	0·1423 (1)	1·03 (4)
	b	0·20047 (7)	0·35510 (5)	0·1422 (1)	0·93 (2)
C(6)	*a*	0·30110 (9)	0·57471 (6)	0·2629 (1)	1·06 (4)
	b	0·30146 (7)	0·57459 (5)	0·2628 (1)	1·00 (2)
C(7)	*a*	0·5241 (1)	0·60484 (7)	0·2484 (1)	1·23 (4)
	b	0·5239 (8)	0·60513 (6)	0·2478 (1)	1·21 (2)
C(8)	*a*	0·59320 (1)	0·53046 (8)	0·3181 (2)	1·51 (4)
	b	0·59326 (9)	0·53014 (6)	0·3183 (1)	1·45 (3)
C(9)	*a*	0·39816 (1)	0·66519 (7)	0·4632 (1)	1·49 (4)
	b	0·39824 (9)	0·66489 (6)	0·4634 (1)	1·45 (2)
C(10)	*a*	0·3549 (1)	0·75361 (8)	0·4284 (2)	1·93 (5)
	b	0·3547 (1)	0·75369 (7)	0·4285 (2)	1·89 (3)

tetraethyl compound than in tetramethyl one. The two halves of compound (2) at 105 K are not as similar as those at room temperature. The thermal parameters of compound (1) at 138 K decrease, on average, to 50% of those at room temperature; those of compound (2) at 105 K decrease to 30% of the room-temperature parameters.

The deformation density distributions on the N—C=S planes of (1) and (2) are shown in Fig. 2. The two halves of compound (2) show practically the same features. The shorter C—N bond gives greater density accumulation (0·5 e Å^{-3}) at the midpoint of the bond than is observed for the longer bonds (0·3 e Å^{-3}). The C=S double bond gives 0·4 e Å^{-3} whereas the C—S single bond is 0·2 e Å^{-3}. There is little density accumulation along the S—S bond. Lone-pair electron density is apparent around all the S atoms. The features around bridged and terminal S atoms are different; the residual density of S(2) (bridged) in (2) shows two peak maxima of 0·4 e Å^{-3} [on the plane perpendicular to the C(5)—S(2)—S(3) plane] about 0·4 Å away from the S atom, making a T_d arrangement with the S(2)—C(5), S(2)—S(3) bonds (see Fig. 3). The lone pairs at the terminal S atom, S(4), have two maxima in the plane of C(6)—N(2)—S(4), about 0·7 Å away from the S atom making a T shape with the C(6)—S(4) bond. There are similar features around the other terminal S atom, S(1). The deformation density along the ethyl C—C bond shows density accumulations at the midpoint of the bond as expected (Wang, Tsai, Liu & Calvert, 1985). Fig. 4 shows the density around the S(4) atom in a plane perpendicular to the C(6)—S(4) bond.

Discussion

The geometries of both compounds at low temperature are the same as those at room temperature. The bond distances are lengthened somewhat at low temperature owing to the thermal-motion difference (Busing & Levy, 1964; Wang, Blessing, Ross & Coppens, 1976). The change in compound (2) is not as uniform, the two halves differing more at low temperature than at room temperature, *e.g.* C(5)—S(2), C(5)—N(1) *vs* C(6)—S(3), C(6)—N(2). The tetraethyl moieties do not change much with temperature. The deformation density

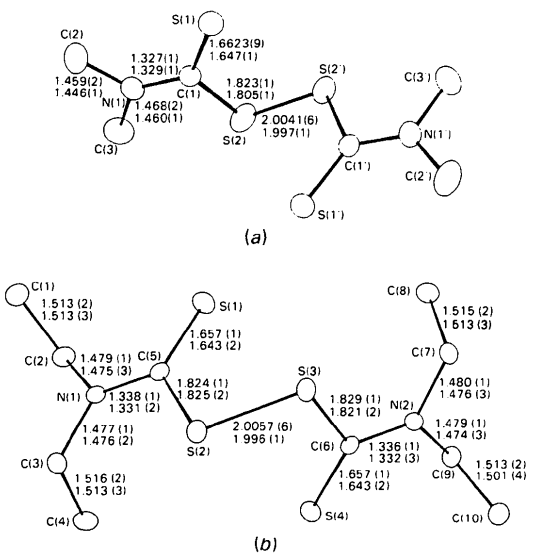
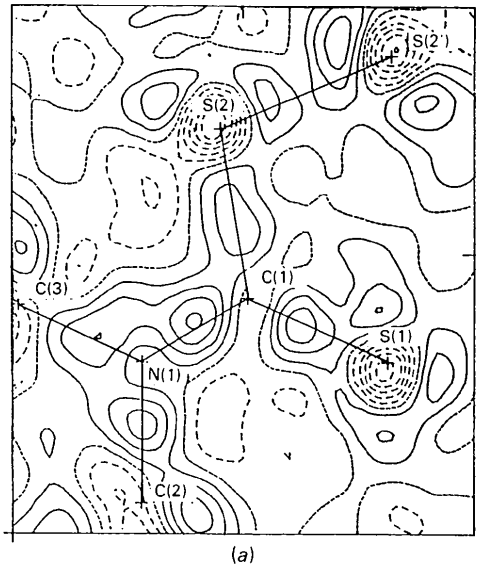


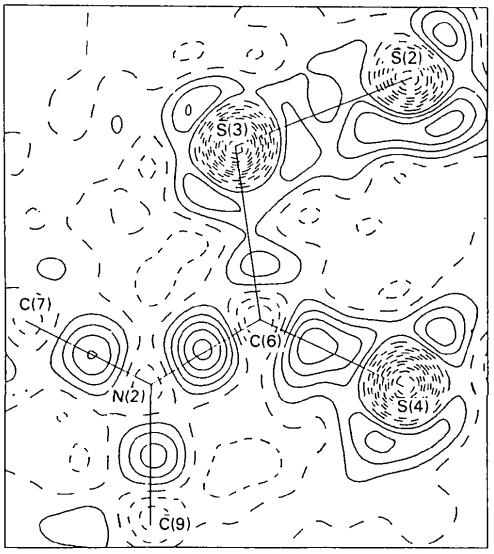
Fig. 1. Molecular structures with bond lengths (Å) at both temperatures for (*a*) compound (1), (*b*) compound (2). Low-temperature distances [138 K for (1), 105 K for (2)] are given above room-temperature distances.

distributions in the N–C=S planes (Fig. 2) are qualitatively the same. This indicates that the electron density distribution of thiuram disulfide is not significantly affected by the alkyl groups on the N atoms. Because of problems with the quality of the data for compound (1), further discussions on deformation density distribution are based on the results obtained for compound (2).

The degree of the density accumulation at the midpoint of bonded atoms follows in the order: shorter C–N > C–C ≥ longer C–N, C=S > C–S > S–S. This order is in accord with those found for other compounds (Dunitz & Seiler, 1983; Wang, Chen & Wu, 1988). There are two different C–S and C–N bond lengths in the same compound. Presumably they represent different bond orders, *e.g.* a single bond for C(6)–S(3), a double bond for C(6)–S(4) and a partial double bond for C(6)–N(2). The residual densities of shorter bond give greater accumulations than the longer ones. The features around S atoms in these compounds are similar to those observed for other sulfur-containing compounds (Wang, Guo, Lin, Kao, Tsai & Bats, 1988; Wang, Chen & Wu, 1988; Cohen-Addad, Lehmann & Becker, 1984) which indicate a substantial electron deficit at the center of the S atom compared with the spherical atomic density in its ground state. In both cases, residual peaks always appear about 0·5 Å away from the S nuclei, as expected for lone-pair electrons (see Figs. 3 and 4). In general, such peaks are also reproduced in theoretical calculations (Breitenstein, Dannohl, Meyer, Schweig, Seeger, Seeger &



(*a*)



(*b*)

Fig. 2. Deformation density maps of (*a*) N(1)–C(1)–S(1) of compound (1), (*b*) N(2)–C(6)–S(4) of compound (2). Solid lines positive and dashed lines zero and negative contours; contour interval 0·1 e Å^{-3}.

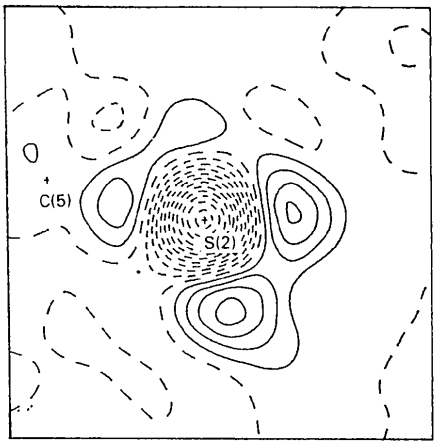


Fig. 3. Deformation density map in the plane bisecting the C(5)–S(2)–S(3) angle, with the projection of C(5) in the plane indicated; contours as in Fig. 2.

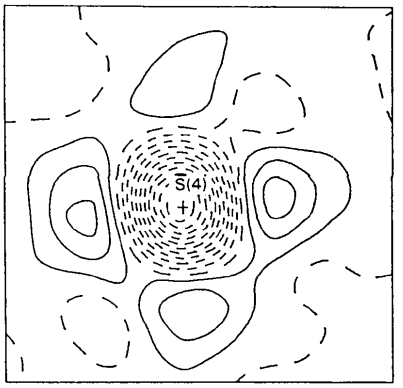


Fig. 4. Deformation density map around S(4) in a plane perpendicular to C(6)–S(4), with the projection of N(2) as the right-hand side of the horizontal axis; contours as in Fig. 2.

Zittlau, 1983; Becker, Cohen-Addad, Delley, Hirshfeld & Lehmann, 1986). The deformation density along the S(2)–S(3) bond is peculiar and quite similar to the S–S–S region in thiathiophthene (Wang, Chen & Wu, 1988). This may be rationalized by recent MO calculations (Kunze & Hall, 1986, 1987) which showed that a valence-electron-rich atom like O, S or F tends to have little density accumulation in the bonding region, if the spherical atomic model density is subtracted.

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References

BECKER, P., COHEN-ADDAD, C., DELLEY, B., HIRSHFELD, F. L. & LEHMANN, M. S. (1986). *Applied Quantum Chemistry*, edited by V. H. SMITH JR, H. F. SCHAEFER III & K. MOROKUMA, pp. 361–373. Dordrecht: D. Reidel.

BREITENSTEIN, M., DANNOHL, H., MEYER, H., SCHWEIG, A., SEEGER, R., SEEGER, U. & ZITTLAU, W. (1983). *Int. Rev. Phys. Chem.* **3**, 335–391.

BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.

COHEN-ADDAD, C., LEHMANN, M. & BECKER, P. (1984). *J. Chem. Soc. Perkin Trans.* 2, pp. 191–196.

CUMMINGS, A. D. & SIMMONS, H. E. (1928). *Ind. Eng. Chem.* **20**, 1173–1176.

DUNITZ, J. D. & SEILER, P. (1983). *J. Am. Chem. Soc.* **105**, 7056–7058.

KARLE, I. L., ESTLIN, J. A. & BRITTS, K. (1967). *Acta Cryst.* **22**, 273–280.

KUNZE, K. L. & HALL, M. B. (1986). *J. Am. Chem. Soc.* **108**, 5122–5127.

KUNZE, K. L. & HALL, M. B. (1987). *J. Am. Chem. Soc.* **109**, 7617–7623.

WANG, Y., BLESSING, R. H., ROSS, F. & COPPENS, P. (1976). *Acta Cryst.* B**32**, 572–578.

WANG, Y., CHEN, M. J. & WU, C. H. (1988). *Acta Cryst.* B**44**, 179–182.

WANG, Y., GUO, L. W., LIN, H. C., KAO, C. T., TSAI, C. J. & BATS, J. W. (1988). *Inorg. Chem.* **27**, 520–524.

WANG, Y., LIAO, J. H. & UENG, C. H. (1986). *Acta Cryst.* C**42**, 1420–1423.

WANG, Y., TSAI, C. J., LIU, W. L. & CALVERT, L. D. (1985). *Acta Cryst.* B**41**, 131–135.

Acta Cryst. (1989). B**45**, 69–77

Crystallochromy as a Solid-State Effect: Correlation of Molecular Conformation, Crystal Packing and Colour in Perylene-3,4:9,10-bis(dicarboximide) Pigments

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Dedicated to Professor Dr Helmut Dörfel on the occasion of his 60th birthday

Abstract

The crystal structure determination of four pigments is described and their structures compared with those of 14 related perylenes. Crystal data: *N,N'*-bis(4-hydroxybutyl)perylene-3,4:9,10-bis(dicarboximide), $C_{32}H_{26}N_2O_6$, $P\bar{1}$, $a = 4{\cdot}705$ (1), $b = 15{\cdot}002$ (4), $c = 18{\cdot}591$ (4) Å, $\alpha = 109{\cdot}72$ (2), $\beta = 95{\cdot}74$ (2), $\gamma = 92{\cdot}82$ (2)°, $Z = 2$, $D_x = 1{\cdot}450$ g cm^{-3}, $R(F) = 0{\cdot}078$ for 2578 reflections; *N,N'*-bis(6-hydroxyhexyl)perylene-3,4:9,10-bis(dicarboximide), $C_{36}H_{34}N_2O_6$, $P\bar{1}$, $a = 4{\cdot}739$ (3), $b = 17{\cdot}412$ (14), $c = 18{\cdot}991$ (11) Å, $\alpha = 65{\cdot}24$ (5), $\beta = 88{\cdot}42$ (5), $\gamma = 85{\cdot}82$ (7)°, $Z = 2$, $D_x = 1{\cdot}382$ g cm^{-3}, $R(F) = 0{\cdot}107$ for 1588 reflections; *N,N'*-bis(4-ethoxyphenyl)perylene-3,4:9,10-bis(dicarboximide), $C_{40}H_{26}N_2O_6$, $P\bar{1}$, $a = 4{\cdot}934$ (1), $b = 15{\cdot}915$ (4), $c = 18{\cdot}849$ (9) Å, $\alpha = 100{\cdot}17$ (3), $\beta = 95{\cdot}89$ (3), $\gamma = 93{\cdot}50$ (2)°, $Z = 2$, $D_x = 1{\cdot}450$ g cm^{-3}, $R(F) = 0{\cdot}070$ for 2268 reflections; *N,N'*-bis(4-phenylazophenyl)perylene-3,4:9,10-bis(dicarboximide), $C_{48}H_{26}N_6O_4$, $P\bar{1}$, $a = 5{\cdot}291$ (1), $b = 11{\cdot}865$ (2), $c = 13{\cdot}972$ (2) Å, $\alpha = 102{\cdot}35$ (1), $\beta = 97{\cdot}32$ (1), $\gamma = 92{\cdot}71$ (1)°, $Z = 1$, $D_x = 1{\cdot}471$ g cm^{-3}, $R(F) = 0{\cdot}046$ for 1716 reflections. Differently substituted perylene-3,4:9,10-bis(dicarboximide) pigments show closely related absorption spectra in a molecular dispersion such as in polystyrene. In the crystalline state the absorption maxima of the same series of compounds spread over a range of more than 170 nm. This crystallochromic solid-state effect is due to different packings of the individual dye molecules in the crystal, in which the molecules are arranged in stacks. All molecules possess a flat perylene tetracarboxylic diimide moiety with bent side-chain substituents. The steric requirement, the crystal conformation and the mutual interlocking of these substituents is classified

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