cations. In the other compounds all the interlayers are occupied by cations but individual differences in their distributions lead to various symmetries.

We are indebted to Professor R. Nitsche for supplying the crystals and for helpful discussions. All numerical calculations were performed on the Univac-1106 of Rechenzentrum der Universität Freiburg.

#### References

BUCK, P. & NITSCHE, R. (1971). Z. Naturforsch. 265, 731.

- CARPENTIER, C. D., DIEHL, R. & NITSCHE, R. (1970). Naturwissenschaften, 57, 393.
- International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: The Kynoch Press.
- NITSCHE, R. & WILD, P. (1970). Mater. Res. Bull. 5, 419-423.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). X-RAY 70 System of Crystallographic Programs, Version July 1970. Univ. of Maryland.
- WEISS, A. & SCHAEFER, H. (1960). Naturwissenschaften, 47, 495.
- WEISS, A. & SCHAEFER, H. (1963). Z. Naturforsch. 18, 81-82.

Acta Cryst. (1973). B29, 1868

# Stereochemistry of an Unusual Trialkyl Sulfonium Ion. The Crystal Structure of 2,3-Dimethyl-2-butenyl-1,1,2-trimethylpropyl-methylsulfonium 2.4.6-Trinitrobenzenesulfonate

## By W. Barnes and M. Sundaralingam\*

Department of Biochemistry, College of Agricultural and Life Sciences, University of Wisconsin, Madison, Wisconsin 53706, U.S.A.

(Received 19 January 1973; accepted 17 April 1973)

The nature and crystal structure of the product obtained from the reaction of methylsulfonium 2,4,6trinitrobenzenesulfonate with two molecules of 2,3-dimethyl-2-butene has been determined by X-ray methods and the product was found to be the title trialkyl sulfonium salt. The triclinic (PI) lattice parameters are  $a = 13 \cdot 128 \pm 0.009$ ,  $b = 12 \cdot 100 \pm 0.006$ ,  $c = 7.992 \pm 0.003$  Å,  $\alpha = 93.94 \pm 0.04^{\circ}$ ,  $\beta = 102.00 \pm 0.04^{\circ}$ , and  $\gamma = 74.95 \pm 0.04^{\circ}$ . The structure was solved by the heavy-atom technique and refined by full-matrix least-squares calculations to an R value of 0.057 using 3504 observed reflections measured on a diffractometer. Knowledge of the structure of the trialkyl sulfonium ion has led to a suggested mechanism for its formation. The sulfonium ion is pyramidal and it is distorted from 3m symmetry. The C-S<sup>+</sup> bond distances are 1.799, 1.830 and 1.882 Å and increase with increasing bulkiness of the alkyl group on S<sup>+</sup>. The ortho nitro groups of the trinitrobenzenesulfonate anion are twisted by 54 and 61° to the benzene plane while the para nitro group is twisted by only 2.5°. There are a number of intermolecular contacts shorter than 3.4 Å. The shortest contacts are between the trinitrobenzenesulfonate anions.

#### Introduction

In an attempt to synthesize another example of a stable episulfonium salt such as that obtained from the reaction of the olefin cyclooctene with methyl sulfenium trinitrobenzene sulfonate (Pettit & Helmkamp, 1963), the latter was reacted with excess 2,3-dimethyl-2-butene (Carbin & Helmkamp, 1970). Two molecules of 2,3dimethyl-2-butene reacted to give a crystalline product whose structure resisted spectroscopic analysis (Carbin & Helmkamp, 1970). The present X-ray study has unequivocally established the structure of the product (1) and has also led to the proposal of a probable reaction mechanism for its formation. A paper on the details of the chemical work and a brief report on the X-ray structure have been published elsewhere (Carbin, Helmkamp, Barnes & Sundaralingam, 1972).

#### Experimental

Colorless crystals of (I) grown in nitromethane and ether were supplied by Carbin & Helmkamp. The crystal data are as follows:  $C_{19}H_{29}N_3O_9S_2$ , triclinic,  $P\overline{1}$ , Z=2;  $a=13\cdot128\pm0\cdot009$ ,  $b=12\cdot100\pm0\cdot006$ ,  $c=7\cdot992$  $\pm0\cdot003$  Å,  $\alpha=93\cdot94\pm0\cdot04^\circ$ ,  $\beta=102\cdot00\pm0\cdot04^\circ$ ,  $\gamma=$  $74\cdot95\pm0\cdot04^\circ$  (obtained by least-squares fit of eleven reflections measured on a diffractometer),  $D_{obs}=1\cdot412$ g cm<sup>-3</sup> (by flotation in CCl<sub>4</sub> and C<sub>2</sub>H<sub>5</sub>P<sub>2</sub>O),  $D_{calc}=$  $1\cdot406$  g cm<sup>-3</sup>. The crystal data are consistent with the presence of one formula unit of the complex,  $(C_{13}H_{27}S)^+(C_6H_2N_3O_9S)^-$  in the asymmetric unit of the structure. The calculated linear absorption coefficient for Cu K $\alpha$  radiation is 24·2 cm<sup>-1</sup>.

The crystal used for the data collection was a plate of approximate dimensions  $0.25 \times 0.05 \times 0.7$  mm. The intensities of 3990 independent reflections were measured on a Picker four-circle diffractometer using nickel-

<sup>\*</sup> To whom correspondence should be addressed.

# Table 1. Observed and calculated structure factors

The data are separated into groups having common k and l values. The three columns of each group list values of h,  $10F_o$  and  $10F_c$  in that order. An asterisk indicates a reflection less than  $1.5\sigma$ , where  $\sigma$  is the standard deviation in the intensity.

Hy-19,0 1 6H 61 2 99 91 Hy-19,0 1 36 37	J 733 -746 S 773 -776 4 276 -117 5 134 145 3 146 145 J 346 151 4 124 121 4 124 121 4 124 121 4 124 121	7 16 -18 7 16 -19 8 46 45 4 17 -27 Ma-14, 1	H, -4, 1 -14 42 44 -14 104 -3 -13 44 45 -12 134 151 -11 44 45	-4 408 -481 14 24 -4 66 -85 -3 100 -106 m, -7 148 -117 -1 485 -468 -4 11 0 625 -478 -8 90 1 198 492 -1 148 2 479 -400 -4 73	-11 6 61 6 6 66 6 1, 1 6 74 7 7 6 9, -4% 2 67 - 177 -23 61 -6 46 -17 100	H, -7, 1 -14 66 A4 -16 121 114 -15 A9 -1 -17 41 6 -11 14 116	-2 201 174 -1 144 -144 0 212 220 1 44 41 2 140 -242 5 45 -42 4 141 445	4 140 -144 4 87 -47 7 47 47 8 08 1 9 39 -17 4, 11, 2	-7 100 -201 -4 174 -182 -7 42 -17 -6 416 -180 -1 447 -441 -2 281 -244 -1 167 327	H, J, S -17 17 -44 -17 13 70 -11 AM 7 -10 49 -103	-6 63 -69 -6 1395 A -6 196 110 -1 76 41 -7 76 -17 -1 146 18 7 66 -49	2 46 -64 3 22 -17 4 148 148 4 47 -47 6 48 3 7 19 14 4 175 7	• 71 - • • • 71 - • • 11 77 - 7 •• 1. •
2 44 -44 1 124 -4 2 11 49 	11 74 74 12 96 -61 13 164 -198 16 36 -61 H. 1, 0 0 516 -519		-19 44 78 -8 288 121 -9 227 217 -6 27 75 -6 283 98 -9 283 98 -9 283 98 -9 46 -9 46 -9 46 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -1 -	4 207 -448 -4 12 4 207 201 -4 40 5 110 -118 -1 116 4 107 -492 -1 12 7 03 -78 -1 46 6 107 - 48 9 107 - 492 10 101 -78 2 7 10 101 -78 2 7 11 25 -58	74 -11 44 -4 49 -10 111 -11 174 -9 197 -16 -1 -8 197 -16 -1 -1 -17 -16 -14 -7 44 -2 -14 -7 44 -2 -14 -4 181 -17 14 -4 18 -1 -1 -14 -4 18 -1	-10 148 118 -8 67 647 -8 748 107 -7 86 -48 -6 148 -118 -6 176 -176 -1 447 601	1 174 -186 3 174 -186 3 18 -18 3 40 -47 10 103 -195 11 43 -46 17 8.4 3 11 43 -46 11 43 -46 11 43 -46 11 43 -46 11 43 -46 11 43 -46 11 4 11 4 1	-1 11 -24 - 124 -124 1 24 -22 2 14 -17 3 40 -47 4 90 -47 4 90 -47 4 90 -47 4 90 -47 4 90 -47	1 744 -714 2 767 -194 1 74 -71 4 75 -18 4 77 -47 4 77 -47 5 47 -47 7 46 41 8 87 -47	-7 141 137 -7 144 144 -6 246 -193 -4 246 -193 -4 246 -193 -9 141 -141 -7 144 351	2 A1 23 + +7 40 + 24 - 24 + 140 + 140 + 31 31 7 141 - 14 + 40 + 40 + 31 21 - 14 + 31 - 14 - 15 - 14 - 15 - 15	H, -A, 4 -14 13# -11 -13 10 -84 -17 41 -49 -11 120 -110 -19 242 -241 -2 118 -111	-17 47 -44 -11 44 -46 -10 47 -47 -7 70 -47 -7 70 -47 -7 71 70 -4 117 31
1 176 12 4 160 -152 5 16 -15 5 16 -15 5 10 -15 1 25 1 26	1 07 11 7 175 176 1 164 185 4 114 -155 4 114 -155 5 184 191 7 64 15 7 64 15 7 64 15	-7 17 16 -6 119 13 -6 61 19 -16 -6 61 19 -7 61 -63 -7 61 -63 -7 61 -63	-1 437 424 n 248 225 1 106 48 2 37 225 3 51 45 4 4 4 202 212	12 47 -11 4 147 13 74 -73 4 4 14 18 -13 4 1 7 24 -13 1 4 1 1 7 24 -13 4 1 7 25 4 2 1 7 -14 22 -21 10 11	174 -2 34 -2 A1 -1 243 -1 4 -1 243 -1 -17 -1 44 -2 -17 -1 44 -2 -17 -1 44 -2 -11 - 1 44 -2 -11 - 1 44 -2 -11 - 1 44 -2 -11 - 1 44 -2 -1 -1 -1 -2 -1 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2	-1 At4 444 0 174 -34 1 44 444 2 170 171 1 171 412 4 114 -4 4 240 147	n, t, ) -17 st -40 -10 17 - 1 -10 17 - 1 -4 st -48 -4 st -48	#1-13, 3 -1 34 -38 -7 70 70 -4 78 -38 -9 48 -48	• • • • • • • • • • • • • • • • • • •	n 144 200 1 147 199 2 247 244 4 444 444 4 146 114 4 44 49 6 131 124 7 21 25	10 44 44 11 12 10 10 14 10 10	-* 61 -*7 -7 184 -*74 -4 17 -76 -4 18 -76 -4 18 -76 -4 67 19 -7 44 -49 -7 79 -198	-4 193 184 -3 131 110 -3 2-7 204 -1 683 651 -1 68 76 1 68 76 2 266 261 4 761 265
1 1 1 1 1 1 1 1	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	1 79 78 Hu-17, 1 -11 55 -55 -10 56 -60 -9 76 -11	7 A1 A1 A A0 -42 A 11A 11A 10 44 47 11 14 17 Hs -44 1	-12 46 43 12 14 -11 43 46 13 14 -10 24 -25 -0 88 40 -7 246 -261 48 16 -7 246 -261 48 16 -4 85 84 -7 23	147 - 4 4 - 4 14 - 14 49 - 4 - 14 - 12 100 - 4	7 210 465 8 110 112 9 126 122 10 115 120 11 115 120 11 11 12 12 40 -16 11 -17	-4 717 -774 -4 114 10 -4 144 440 -3 144 440 -7 145 784 -7 49 -74 -1 49 -74 -1 49 -74	-7 00 0 -1 117 -116 -10 104 11 -10 104 11 -10 11 10	-17 47 14 -11 74 74 -4 77 44 -4 11 11 -7 41 -11 -4 777 74 -4 777 74 -4 777 74	9 21 -29 9 40 - 21 19 121 - 11A 11 27 - 13 12 74 -27 13 44 47 14 44 47	-1 134 141 -2 161 162 -1 16 664 1 186 -161 1 167 161 2 126 126 1 10 21 6 167 167	1 101 -107 1 171 -117 1 187 -197 1 44 - 4 4 119 -174 4 147 -147 4 74 7. 7 44 -44	• 197 -721 • 125 - 110 • 141 - 141 • 20 -11 • 21 - 20 11 - 54 - 4 12 - 12 - 11
1 144 144 2 148 144 1 112 124 4 75 - 20 4 67 - 20 4 67 - 20 7 94 201 8 06 - 2	0 741 747 11041 1048 2 16 -49 3 184 184 4 100 87 5 184 187 6 27 -33	-7 19 -[6] -4 78 -77 -4 47 46 -4 14 15 -7 140 -144 -7 140 -14 -1 74 -77 - 67 -41	-14 24 -27 -14 14 -27 -13 4 -11 -17 43 -47 -11 44 -44 -10 23 24 -4 48 47 -8 48 -103		-46 -11 19* -16 -47 -10 19 -7 -44 -9 147 14 -116 -8 48 -8 49 -7 148 -21 44 -4 48 -4 161 -4 48 -4 161 -4 48 -4 161 -4 48 -4	-14 80 -14 -14 40 -14 -14 40 -14 -17 48 24 -17 48 44 -17 48 44 -17 48 44 -17 48 44 -17 48 44 -17 48 44 -17 48 44	2 244 - 224 3 43 - 45 4 170 - 110 4 211 - 142 4 211 - 244 4 211 - 244 4 211 - 244 4 214 - 244	-7 74p 81 -4 11 -40 -4 14 11 -40 -4 14 11 -40 -7 11 -40 -7 11 -40 -7 11 -40 -7 12 -7 70 -7	-1 44 -1 -2 21 -10 -1 204 -148 9 76 43 1 117 202 2 271 745 1 36 26	-11 34 31 -17 70 -78 -11 107 -105 -11 109 - 6 -1 80 -17 -4 104 -115 -7 104 114	4 144 141 7 44 74 4 79 191 7 41 41 1 74 19 7 74 7	H, 24, 4 -14 7H 4 -17 71 41 -17 42 24 -11 44 44 -10 47 77	H. 7. 6 -11 8C 76 -12 79 -71 -13 187 -114 -10 107 -101 -0 160 -160
H, -#, A 1 341 192 2 18 4 1 81 -69 4 136 120 5 202 193	4         47         47           0         48         87           10         20         16           11         21         16           12         144         167           13         144         167           14         16         167           14         16         167           14         16         167	3 /0 -4 1 40 4 4 116 -120 me-11e 1 -12 16 -18 -11 12 26	-6 01 105 -5 140 -610 -5 140 -810 -5 226 221 -7 217 481 -1 101 -176 - 406 -610 1 112 111	4 744 -541 4 214 4 744 -541 4 214 4 145 164 4 4 24 1 145 164 4 174 4 105 164 7 4 17 10 53 67 4 18 11 122 -115 16 16 14	-17 -1 174 -11 -276 -2 64 -4 -47 -1 176 -14 -47 -1 176 -14 -11 - 147 -4 -11 - 147 -4 -11 - 147 -4 -14 -14 -14 -14 -14 -14	-* 184 -161 -* 184 -161 -* 184 -161 -* 197 -167 -* 197 -167 -* 197 -167 -* 197 -167 -* 197 -167 -* 197 -167 -* 197 -167	10 100 110 11 00 -7 17 107 17 1040 10 1040 1040 107 11 77 -76	1 21 24 2 78 76 Hs-11s 1 -12 22 22 -11 16 -12 -10 72 48	4 110 133 4 10 -21 7 214 -263 4 62 40 4 62 40 4 63 40 11 6 10	-4 144 -417 -4 447 -487 -7 211 -187 -7 24 16 -1 48 51 -1 15 1 141 15 2 89 -87	-1 14 17 -4 74 49 -1 16 -16 -7 175 -173 -1 164 -15 - 144 -7 -4 -4 -4 -4 -5 -4 -5 -4 -4 -5 -5 -4 -4 -4 -4 -4 -4 -4 -4 -4 -4	-4 140 144 -4 25 21 -7 14 35 -4 141 124 -5 21 9 -6 154 -111 -7 217 -217 -7 105 97	-* 11** L -7 10 -61 -6 110 -107 -0.381 -797 -4 17* -186 -7 36 -3* -7 1** *1 -1 1*1 -188
4 74 76 7 111 114 4 174 144 4 27 41 He -7, 4 1 44 14 1 44 14 14 14 14 14 14 14 14 14 14	H. 4. 0 -14 20 40 1 447 -410 1 447 -410 1 447 -410 1 447 -410 1 447 -410 1 447 -410	-10 22 41 -10 22 41 -1 40 -19 -7 23 -24 -4 159 -11 -1 159 -11 -1 159 -11 -1 159 -11 -1 159 -11	2 474 -444 4 474 -444 4 207 -545 4 28 -11 4 266 -227 7 18 -4 4 4 4 4 76 -15	-11 40 40 -1 11 10 -11 40 40 -1 11 10 -11 40 40 -1 11 40		1 144 -114 1 149 -294 1 149 -294 4 144 -114 4 144 -114 4 21 -98 -117 8 202 -101	-1 14 141 -4 106 111 -7 117 144 -4 47 47 -4 44 47 -5 124 -117 -7 46 111		-14 11 11 -14 113 111 -14 113 111 -17 10 11 -11 12 124 -17 41 41 41	* 14 -13 * 141 -148 * 141 -148 * 241 -248 * 241 -248 * 141 -247 * 34 - 34 * 141 -147 * 144 -14	· · · · · · · · · · · · · · · · · · ·	1 14	- +7 FI 1 JAT 743 7 84 61 1 144 -144 4 44 10 4 70 21 7 74 -20 8 40 - 40
1 74 44 4 91 -01 4 115 -115 1 15 -11 1 16 -17 1 16 -7 3 74 -76 1 27 -75 2 37 -75	A 117 144 7 148 15 4 40 -1/19 10 217 218 11 148 1 12 128 -31 13 22 20	-1 124 -110 -1 124 -10 -1 124 -12 -1 124 -12 -1 124 -12 -1 124 -12 -1 124 -12	10 47 44 17 49 -4 17 49 -4 18 -1, 1 -14 15 14 -14 41 -20	-10 1/4 1/4 -1 1/4 -1 1/4 -0 1/4 1/4 -1 1/4 -7 114 1/4 -1 1/4 -7 114 1/4 -1 1/4 -4 1/4 -1 1/4 -1 1/4 -4 1/4 -1 1/4 -1 1/4 -4 1/4 -1 1/4 -1 1/4 -1 1/4 -4 1/4 -1 1/	-40 -11 47 4 -50 -11 47 6 -10 -11 47 6 -11	4 117 157 17 A0 18 11 14 -10 11 44 41 11 47 41	-1 56 60 3 57 647 1 136 117 2 110 156 5 100 521 6 251 -288 6 161 166	4 114 176 1 115 125 2 41 16 1 116 125 4 1 16 1 16	-8 193 601 -7 105 79 -4 79 -81 -4 175 150 -6 176 194 -7 119 -111 -7 418 -479 -1 107 776	12 14 141 14 24 14	-1 141 -111 -7 70 -7 -1 67 -47 - 86 -97 1 17# -17 7 76 -11 1 97 -91		• 47 .47 10 80 .14 11 140 14 12 47 41 41 9. 6 +11 23 .29
44. 7 1 741 -274 2 708 101 1 41 -41 4 334 -347 4 116 -111	14 71 74 14 64 8 1 245	-11 16 18 -12 68 52 -14 106 10* -11 106 10* -11 108 13 -9 58 60 -6 90 91	-12 156 -155 -11 25 16 -10 226 -223 -9 226 -223 -9 78 -98 -7 23 26 -6 17 -55 -5 196 -202	-1 117 116 1 17 0 01 -117 17 17 1 446 447 1 4 7 706 777 4 7 107 170 4 1 706 777 4 1 107 170 4 1 107 170 4 1 10 17 1 107 170 4 1 11 10 4 1 11 10 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	-74 -7 11 -74 -44 -7 11 -77 -44 -7 11 -77 -44 -7 11 -77 -44 -77 -41 -77 -41 -77 -41 -77 -41 -77 -41 -77 -41 -77 -41 -41 -77 -11 -41 -11 -41 -11 -41 -11 -41 -11 -41 -11 -41 -41 -41 -41 -41 -41 -41 -41 -41 -41	-17 101 -40 -17 101 -40 -11 71 -71 -10 4 41 -10 4 -10 -10 4 -10		-17 - 57 - 57 -11 - 11 - 57 -16 - 54 - 54 -16 - 54 - 54 -17 - 54 - 55 -18 - 51 -18 - 51 -19 -19 -19 -19 -19 -19 -19 -19 -19 -19	1 110 111 2 104 101 2 104 101 4 104 101 4 104 101 4 104 107 1 100 100 100 1 100 100 100 100 1 100 100 100 100 100 1 100 100 100 100 100 100 100 100 100 1	-4 14 14 -4 44 -41 -4 741 -747 -4 144 -14 -4 144 -14 -4 144 -14 -4 144 -	- 17 - 17 - 17 - 17	-11 17 -11 -2 24 -24 -4 24 -44 -4 14 -44 -4 41 -44 -4 14 -44 -4 14 -44	-17 47 -46 -11 47 -45 -10 774 -176 -4 77 -176 -4 77 -46 -5 17 -46 -5 14 -167 -6 147 -164
7 [A4 -]48 8 [A4 -]49 9 []7 -]07 10 A4 -60 11 14 -34 H4 -4, 0	* 147 -143 * 147 -143 7 55 -48 * 118 -48 * 118 -48 * 118 -195 10 141 -195 11 175 -175		-4.404 -419 -11/47 -1380 -2.471 481 -1.437 -431 0.742 -248 1.837 -748 2.102 -122 4.144 144 4.201 -122	7 21 14 8 352 327 m, 1 4 81 76 10 89 1 4 4 11 19 27 45 50 12 756 350 - 4 50 15 56 57 - 1 42 16 68 -7 -7 5 5 5	• A 0			-4 38 4 -3 45 -48 -3 168 -187 -1 71 74 5 74 -35 1 74 -117 7 18 -117 7 18 -117		A 184 -117 1 414 -414 1 414 -414 1 16A -114 4 104 -107 4 104 -107 4 104 -107 4 104 -107		-7 47 -71 -1 48 47 9 144 190 1 44 -46 7 47 46 7 47 46 1 77 14 4 191 1 94 1 95 1 95	-3 26 -23 -2 400 -176 -1 25° -146 5 25 29 1 45 -29 2 167 -176 • 91 -276 • 94 -150
1 141 102 2 107 -240 1 204 -170 4 204 -170 4 204 -170 4 204 -170 1 4 1-170 1 4 1-170 1 1 1 4 0 1 10 1 10	12 43		4 184 -198 6 187 -187 7 198 - 4 8 86 - 41 9 119 - 116 10 167 -150 11 88 - 85 12 86 - 85		04         -14         14         1           -24         -11         76         1         76           -41         -17         76         1         1           -11         -11         14         14         14           -64         -10         41         44         44         14           -64         -10         41         44         44         14         14           -64         -10         41         44         44         21         24	4 117 -112 4 210 -112 4 210 -112 4 110			-12 14 14 -13 00 8 -14 25 24 -0 26 16 -0 361 -240 -7 321 -240 -7 321 -140 -4 368 -342			1 17 4 1 17 4	• 714 274 • 84 84 • 147 29 • 141 24 11 85 8 11 85 8 12 80 80
10 1444 -11 11 A1 47 12 A7 45 He -6, 0 1 47 -30 2 171 -144	4 62 35 5 735 - 736 6 115 - 111 7 139 - 10 8 179 - 186 9 355 - 551 10 155 - 125	-13 27 31 -12 28 -4 -11 52 -51 -16 33 56 -4 136 146 -4 68 -2 -7 186 78 -6 173 175	Ha =2+ 1 -14 44 -44 -14 44 -44 -11 140 14 -12 16 -48 -13 16 -16				4 14 -14 4 74 144 4 74 144 1 14 14 1 4 11 1 14 11 1 15 11 1				-1 10 47 -1 10 47 -1 40 47 -1 40 47 -1 40 47 	-11	
1 916 - 121 4 243 247 4 114 114 4 383 483 7 162 145 8 35 38 9 104 -4 10 114 117	17 11 -74 18 17 -74 18 170 -1 19 -10 19 -10 19 -10 19 -10 19 -10	-4 [30 105 -4 28 81 -1 281 282 -2 18 14 -1 122 -327 - 146 -11 1 244 240 2 48 48	-10 4g 8 -9 129 131 -9 129 131 -9 129 131 -9 129 132 -9 129 131 -9 129 132 -9 129 131 -9 129 132 -9 129 129 -9 129 132 -9 129 19 -9 10 -9 10	3 100 107 -2 114 1 101 101 -1 10 4 60 -07 1 0 40 4 717 -2311 1 7 7 10 20 7 1 11 7 10 20 4 1 4 10 -14 6 10 -1 4 10	110         2 Au         2 Au         2 Au           11         5         6         71         71           71         6         7206         70         70           105         7         6         6         70           105         7         6         6         70           105         7         6         6         70           105         7         6         6         70           105         7         6         6         70           105         7         6         6         70           105         7         6         6         6	-14 14 -0 194 1-4 -0 194 -7 754 -7 754 -7 447 447 -4 407 453 -4 407 453 -4 554	••, •, )	2 2 1 3 4197 1 31 -477 3 138 -417 3 138 -417 4 14 -417 4 14 -417 4 14 -417 4 14 -417 4 15 -47 4 19 -47 4 1	4 194 311 4 10 47 7 45 44 8 10m 17 9 374 321 10 140 141 11 17 -17 17 78 39	-	-4 47 -41 -4 48 -41 -7 28 -18 -4 72 -19 -4 12 -19 -4 12 -19 -4 12 -19 -1 -19 -1 -19 -1 -19 -19 -19 -19 -19 -19 -19 -19	-+ 44 40 -9 48 85 -* 489 445 -1 149 -45 C 339 -354 1 146 -*** 7 196 -15 7 196 -15	-+ 36 [4 -+ 256 -14 -5 256 -181 -5 351 -15 -1 17 -27 - 147 -25 - 147 -25 - 246 -49
13 44 1 1 5/0 440 2 34 -244 1 142 -171 4 46 107	3 164 145 4 74 11 5 114 134 6 134 137 7 94 -79 8 54 -63 7 54 52 10 76 -28	4 134 140 4 147 141 4 147 141 4 147 141 4 14 14 4 14 14 14 4 14 14 14 4 14 14 14 14 14	-1 267 348 n 70 111 1 013 -010 2 11 -17 1 404 457 4 206 100 9 217 220 6 207 -200	11 131 126 7 26 12 41 60 4 11 13 77 76 4 44 14 77 75 10 26 H+ 4+ 1	44 m, sty 7 114 sty sty 7 114 sty sty 1 11 -14 7 11 -14 7 11 -14 7 11 -14 7 11 -14 1 14 -17 1 14	-1 196941 A 416 - 401 1 116 - 401 2 106 - 411 4 117 - 139 4 16 - 417 4 16 - 417	-1 16 -14 -1 16 -16 1 160 -14 -1 49 -19 -1 49 -19 -1 49 -19 -1 41 -11	H, 14, 1 -19 MB -11 -19 MB -11 -19 MB -4 -11 47 44 -11 47 44 -10 14 -13	***     -1*     1       -1*     1*     -1       -1*     -1*       -11     7*       -10     -1*       -10     -4*       -11     7*       -10     -4*       -10     -4*				4 22 22 22 4 22 22 22 4 22 22 22 4 22 4 22 22 4 2 4
6 74 -76 7 158 -155 8 176 -155 8 169 -155 1 169 -156 11 45 -151 11 45 -15 12 17 18	12 140 10 13 07 106 14 24 -11 H, 4, 6 1 15 112 1 15 112	-10 179 -11 -11 179 -11 -12 47 -59 -11 48 62 -10 171 171 -5 17 11 -7 19 -18 -6 10 -76	4 174 186 9 24 -92 10 195 -198 11 194 -184 12 42 -184 13 44 -184 14 10 19 10 19 10	-11 167 -170 7 71 -10 128 -1 1 6 -7 47 61 1 1 6 -7 47 61 3 1 6 -7 117 -117 6 46 -7 117 -117 6 46 -4 68 -66 9 -5 115 -116 7 62	1         -1         40         -4           5         -1         1         -7           1         -1         1         -7           4         -4         1         -4           -4         -4         1         -4           -6         -4         1         -14           -6         -4         1         -14           -7         -4         1         -4           -7         -4         1         -4           -7         -4         1         -4           -7         -4         1         -4           -7         -4         1         -4           -7         -4         1         -4           -7         -4         1         -4							-16 44 64 -11 167 -176 -11 67 -176 -11 67 -176 -11 67 -176 -11 67 -176	12 42 44 He 44 4 -11 41 44 -14 44 -14 47 -17 104 2 -17 1 -11
H, -3, 0 1 734 -747 2 431 -448 1 347 -344 4 431 -144 1 91 -142	2 74 72 1 A4 28 4 104 161 4 104 109 4 104 100 4 104 100 4 104 100 4 104 100 4 104 100 4 100 1000 4 100 1000 4 100 1000 4 100 1000 4 1000 1000 4 1000 1000 4 1000 1000 4 1000 1000 100000000000000000000000000	-5 40 48 -4 123 124 -7 106 -106 -2 102 -106 -1 46 -54 0 113 -97 1 101 -290 2 135 -129	-14 77 75 -13 69 66 -12 30 28 -11 273 265 -10 122 135 -10 122 135 -10 137 -129 -4 156 568	-2 103 101 -1 106 -102 #+-1 0 403 -103 #+-1 1 80 27 -0 24 2 202 -255 -4 51 3 812 -182 -3 84 6 400 -606 -6 76 9 8 10 -5 10	· 7 701 - 774 · 7 1 704 - 704 · 7 1 714 - 704 · 7 10 - 77 · 10	-14 44 47 -14 14 10 -13 08 4 -11 134 11- -10 201 -51 -0 154 554 -4 118 112		1 111 2 74 27 4 101 111 4 40 44 4 51 24 4 51 24 4 60	1 107 -284 2 161 -101 1 16 -12 6 27 18 4 366 -286 7 316 225 6 4 4 -1		-1 66 63 -1 66 20 1 61 64 2 76 -21 4 47 -63 4 776 14		
1 144 - 147 7 144 - 147 8 147 - 148 9 187 - 176 19 227 - 271 11 14 - 27 12 49 - 47 11 29 - 8	11 11 12 11 17 12 11 17 12 11 17 12 11 17 12	+ 4477 + 187 -700 + 67 -90 7 11 -11 8 78 -77 + 70 -64 H+ -7+ 1		a 40 -41 -6 VA 7 143 -132 -2 134 8 45 -457 -2 47 9 79 -7 -1 43 10 45 -83 -410 11 20 25 1 74 12 149 -12 13 24 -18 He-12	-144 6 47 -41 -144 6 47 -41 -447 10 43 -43 -44 11 149 11 -144 -20 He -44 2 -14 24 24 -14 24 24		- 1 44 - 294 - 1 44 - 144 1 - 11 - 249 2 244 - 296 4 237 - 216 4 114 - 297 4 45 - 294 4 145 - 294 7 216 - 119	H, -1, 1	· · · · · · · · · · · · · · · · · · ·	1 441 474 4 774 744 4 77 744 4 77 744 7 147 124 4 174 174 4 174 174 10 147 101	u, -1, -2, -2, -2, -2, -2, -2, -2, -2, -2, -2	- 74644 - 744176 - 18 -17 - 19 -17 - 19 -17 - 19 -17 - 1917 -	* 1246 * 4211 149 # 242 261 * 44 44 * 76 41 * 75 42 * 46
H1. A 1 447 647 7 114 121 1 178 144 4 68 4 4 408 137 6 108 17	2 47 62 3 18 21 4 178 -4 5 164 -161 4 74 -54 7 18 -1 8 64 69 9 16 -0	-14 78 -87 -13 74 -71 -12 85 44 -11 12 8 4 -10 53 49 -9 144 147 -8 67 -7	2 14 21 4 404 457 4 140 173 4 151 -151 6 59 -69 7 185 190 8 15 11 6 122 121	-11 1a H & & 1 -10 7 -11 10 <sup>4</sup> -11 -7 10 -11 20 <sup>4</sup> -11 -7 11 -10 22 -30 -7 65 -9 60 -65 -6 6 -7 25 25 -6 96 -7 25 25 -6 96	-10	2 43 -42 1 410 -443 4 23 10 4 11 4 11 4 11 4 11 5 111 5 11 5 11 5 11 5 111 5 11 5 11 5 11 5 11 5 11 5 11 5 1	10 40 -49 10 40 -49 11 144 -10 12 144 11 		-12 11 A8 -11 A8 -14 -14 184 -144 -4 20 23 -8 48 A0 -7 15 -21 -4 116 122 -4 16 101	12 44 47 -10 44 -44 -4 44 44 -7 144 11 -7 144 -114	-4 14 -11 -4 44 -11 -4 9 71 -4 144 131 -7 144 141 -1 144 141 1 71 -1 144 74	12 34 34 -14 17 -14 -14 17 -14 -15 As 3 -15 -15	11 a. 41 
4 75 -81 4 90 90 10 72 -65 11 16 -61 17 66 51 17 66 51 18 62 -65	He 11+ 0 He 11+	-6 222 -224 -5 66 -60 -6 665 -60 -7 298 -279 -7 72 -75 -1 0° 16 0 268 -250 1 106 -279	11 17 8 12 14W -10 13 83 77 W. 0.1 -14 47 -48 -13 30 49		-14 -1 14 -14 -74 -1 149 -14 -74 -2 19 -79 14 -1 419 -97 14 -1 419 -91 -14 -1 -14 -14 -1 -14 -14 -14 -14 -14 -14 -14 -14 -14 -14			1 114 1 210 2 710 3 70 4 74 4 144 1 44 4 77 4 74 4 144 1 47 4 144 1 44 1 44	-4 211 200 -1 110 -17 -2 127 437 -1 171 -167 0 437 -663 1 192 -664 2 100 16 1 192 -664 4 40 77	-1 104 -1 10 -1 104 -1 104 -1 10 -1 104 -1	7 119 6 7 7 4 6 46 77 6 18 70 Ha -Ra 4 -11 65 61	-10 0531 -7 2% -20 -8 20 57 -8 10 -1% -5 26 26 -5 10 88 -4 10 88 -4 18 -17 -1 267 -268	-+ + +072 -+ +07172 -+ +07174 +101194 +101194 +101104 +101101 +101 
N. G. 3 1.600 ARL 2.140 -184 3.26 -18 4.466 -09 5.211 207 6.46 32 7.244 203	4 144 -107 4 149 2 4 149 0 4 74 -90 7 21 -18 8 14 1 2 40 -40 10 104 -114 1 41 -47	1 243 -244 4 98 -97 4 21 -15 6 40 -44 7 219 -227 8 148 -15 9 25 21 17 49 -45	-17 114 187 -11 14 -44 -10 117 -173 -4 213 210 -4 114 148 -7 278 -781 -4 93 -45 -4 93 -45	4 13 21 -12 17 4 13 21 -12 17 4 338 -117 -11 48 4 33 -117 -11 48 7 1-1 153 -4 64 8 33 -14 -16 64 1 17 -170 - 67 64 10 107 -107 -6 7 64 11 24 26 -2 67	4 774 -746 4 4 776 -741 4 4 776 -741 4 776 -741 4 776 -741 4 776 -741 5 76 -751 4 776 -751 5 7	-11 300 -57 -10 218 -57 -0 172 178 -8 99 36 -8 99 36 -4 257 -542 -5 48 -58 -4 202 355	7 44 44 6 10 <sup>4</sup> -17 4 73 -101 4 44 -87 4 14 10 7 18 74 4 91 -91 9 17 19	1 44 44 HL -4, 5 -14 40 14 -13 44 -7 -13 111 -110 -11 45 -46	5 4] 87 6 17 14 7 51 -57 8 165 -168 9 108 111 10 56 -58 11 109 -107 12 37 -57	• 141 144 • 141 - 44 • 41 - 44 • 70 - 74 7 • 7 - 61 • 118 167 10 • 6 • 50	-1: 195 413 -1: 195 7 -1: 175 -1: -1: 175 -1: -1: 155 75 -4: 80 7: -7: 155 12 -4: 35 -5 -5: 155 -5 -5: 15	-: 411 474 0 118 -:74 : 207 147 : 163 137 : 174 -:174 4 197 6 48 57 6 64 51	1 44 -67 4 44 -67 5 127 114 4 21 -78 7 714 -78 7 714 -78 7 715 -65 10 80 -85
R 78 0 9 60 52 19 01 46 11 111 111 17 71 -26 13 57 57 16 76 24	12 1mm 11 m, 12, 0 0 cf 1 1 12 -28 2 21 12 1 70 72	H5. 1 -14 11 -12 -14 27 24 -11 10 14 -12 4F -7 -11 47 42	-1 01 114 -2 114 -148 -1 147 -148 -1 147 -146 -1 147 -136 -1 147 -136 -1 147 -136 -1 147 -136 -1 147 -136 -1 147 -125	17 147 -177 -4 176 17 15 -44 -7 4 14 17 -44 -7 4 -1 19 -1 19 -1 7 -1 -1 -1 19 -1 -1 -1 19 -1 1 -1 -1 19 -1 1 -1 -1 1 -1 1 -1 -1	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-7 49 41 -1 140 141 0 41 43 1 348 -334 2 296 243 4 314 367 4 325 -316	-4 -4 -57 -4 -4 -57 -4 -4 -57 -5 -74 -177 -7 -74 -179	-* 1*4 -1** -* **A -*** -* *11 -** -* 107 112 -* 114 -A -* *15 -*08 -* 12* -8 -* *26 -7*7	H: 1: 1 -14 A7 6* -13 101 84 -17 10 77 -11 5M 8 -10 84 -81 -9 47 18	1) 14 -74 H, 4, 1 -4 47 -41 -5 111 -119 -7 11 -114	-1 75 10 -7 178 11 -7 178 11 -1 787 170 1 76 76 1 74 11 7 277 276 1 46 40	1 124 -314 1 141 -344 3 45 -371 10 37 -324 11 40 -34 M1 9, 4 -34 61 47	11 14 - 76 H1 74 4 -10 70 76 -0 20 - 10 -7 78 - 61 -7 78 - 61 -7 28 - 11
H+ 1,0 A 701 240 1 171 170 2 477 586 3 746 -611 4 196 -201 5 474 511 4 192 140	5 76 -2 4 81 41 7 64 67 8 16 71 10 11 16 P4 13, 5	-10 /21 /12 -9 10 -24 -8 11 - 7 -7 186 170 -6 18 -26 -4 184 -47 -4 184 187 -4 184 187 -3 492 411	5 07 -76 6 20 17 7 100 -100 8 12 -10 9 24 77 10 96 101 11 116 -0 12 156 4 13 40 57	-= q7 q3 b 74 -7 67 76 4 60 -4 11 13 -4 260 266 N,-10 -4 16 -51 N,-10 -3 40 B6 -11 26 -7 40 B6 -11 26 -1 92 R4 -11 36 0 133 -116 -10 86	24 -7 140 14 -19 -8 41 14 -7 188 -147 -7 -6 41 -17 -6 41 -17 -6 10 -17 -7 -6 10 -17 -7 -6 10 -17 -7 -1 10 -1 -2 807 -17 -1 -1 40 -441	7 17 -34 8 106 -107 9 340 145 10 109 111 11 91 86 17 78 -27 15 99 77	-1 198 4 9 44 40 1 86 85 2 110 178 9 49 46 4 19 121 4 148 119 4 148 139	-1 202 -244 0 01 101 1 46 -38 2 286 -271 1 165 -171 4 76 72 5 17 -0 6 88 -76	-R 18 -71 -7 27A 24A -4 1A1 172 -5 8% -14 -4 14A -118 -7 25 15 -7 115 205 -1 138 -367 0 606 -343		· · · · · · · · · · · · · · · · · · ·	-11 67 66 -12 67 -66 -11 100 -61 -10 65 15 -10 65 15 -10 65 15 -1 107 107 -1 96 87 -1 107 107 -1 1	-4 174 -177 -4 04 -04 -7 27 19 -7 111 -177 -1 148 -187 0 148 -187 1 41 -76 7 127 -127 1 50
7 144 -144 A 710 -241 7 144 140 10 100 147 11 110 -116 12 47 -48 14 45 14 18 14	0 10 10 1 11 104 2 104 100 3 10 -5 4 106 1 4 106 1 4 106 1	-1 147 142 5 113 174 1 124 111 7 124 144 4 144 4 144 4 144 4 144 -17 -17 -17 -17 -17 -17 -17 -17	16 28 -26 -1. 1. 1 -1. 17 -7 -1. 77 -76 -12 116 -113 -11 A7	1 81 -67 -6 70 2 442 543 -8 94 3 45 -31 -7 76 4 723 -710 -8 16 4 749 -8 44 5 46 341 -6 47 7 164 -158 -1 191 4 71 -41 -2 144	-105 - 107 - 461 -105 - 107 - 617 -105 - 107 - 107 -105 - 107 - 107 -105 - 107 - 107 -107 - 107 -	H, 6, 7 -11 RM 6 -12 6 -48 -11 76 -71 -10 60 17 -0 60 10 -6 24 -750	1 16 84 9 102 100 10 00 0 He 12: 2 -3 10 23 -7 10 38		1 19 -6 2 166 198 1 72 -77 6 147 193 5 170 113 6 178 163 7 171 176 7 243	6 61 -61 9 31 -100 7 100 -97 4 37 34 9 49 61 10 41 -52 11 49 -44	-11 74 -77 -17 59 -55 -9 123 -721 -8 238 -719 -7 51 46 -6 45 19 -4 148 -146 -6 117 -115	-1 41 47 -3 181 165 -2 458 455 -1 172 180 0 178 470 1 457 405 2 370 -758 1 27 25	4 00 -2 4 183 -186 - 183 -186 - 183 -186 - 183 -196 - 197 - 191 -159 - 199 - 1
H. 7. 9 9 171 -139 1 48 -17	7 .5 44 4 45 48 9 70 91 He 14, 7	7 19 10 8 98 -11 9 114 -18 10 10 48 11 11 19	-R 70A -279 -R 70A -279 -7 14 -14	• 127 -126 -1 144 10 120 -26 0 144 11 111 -115 1 04 12 44 40 2 45 13 87 87 1 17	-141 8 747 740 -144 0 148 145 -90 19 44 446 80 11 197 8 -17 17 47 46	-7 48 -48 -4 17 -12 -4 14 14 -4 14 14 -4 14 14	-1 11 10 0 19 21 1 14 -10 2 14 -12 4 18 10	-17 9F -19 -11 123 -120 -10 99 -98 -9 244 -247 -8 149 -191	9 174 -10 10 110 -114 11 47 42 12 64 58 13 20 -27	**, *, * -* ** -**	-1 201 186 -2 70 11 -1 190 -181 0 14 -17 1 94 4	• 570 •76 • 201 •02 • 500 23 7 371 126 8 170 173	

.

stand and a standard a 1997: Standard a standar 1997: Standard a stand	uujees	ининден (	in the second state of the	ייאנווועווויאייייייייייייייייייייייייייי	anonana, anonana, maraa araa araa araa araa araa araa a		<pre></pre>	and a state of the second s Second second	annunt, annunenen annunen annun an a annun annun annunuen annunuen annunuen annunuen annun annun annun annun a ana ana annunganan annunganan an a a annun an a annun annu annunganan annunganan annunganan an an a a annun annun annun annunganan annunganan annunganan annunganan annung	areas ( 1997)		יאינונינייי אוווייייי אינטארטיייי, אווויייין אינעטע אינעטע אינעטעע אינטענעעע אינטענעען אינטעטעע אינעטעעע אינעט אינענענגע אינעטערע אינטעערע אינעטעע אינעטעע אינעטעע אינעטעע אינעטעעע אינעטעעע אינענטענע אינענענענע אינעטעעע אינעטעעע אינעטע אינעטעע אינעטעעע	un , australia , australia , andalian , australian , australian , australian , australian , ais , a , a , a , a 2	1411 - 1411, - 1411, - 1411, - 1411, - 1411, - 1411, - 1411, - 1411, - 1411, - 1411, - 1411, - 1411, - 1411, - 1411 - 1411, -
--	--------	-----------	--	--	---	--	-------------	--	---	---------------	--	---	--	---

Table 1 (cont.)

filtered copper radiation and a  $\theta$ -2 $\theta$  scan to a maximum  $2\theta$  of  $128^{\circ}$ . The scan width was  $1.4^{\circ}$  with background counts of 10 s on either side of the peak. 3504 reflections had an intensity (I) to standard deviation ( $\sigma$ ) ratio of 1.5 and these were included in the final refinement.  $\sigma$  was derived from counting statistics (Stout & Jensen, 1968). After application of the usual Lorentz and polarization corrections, the overall scale factor and temperature factor were determined by Wilson's (1942) method. Absorption corrections were not considered warranted, as the major purpose of this investigation was to determine the chemical structure of the product in question.

# Structure determination and refinement

The structure was determined by the heavy-atom technique. The positions of the two sulfur atoms were derived from a three-dimensional Patterson map. For economic reasons we initially used only the strongest 2697 reflections with an  $I/\sigma$  ratio greater than 15.5. Several successive difference Fourier syntheses provided the approximate positions for all of the nonhydrogen atoms. The conventional  $R(=\sum ||F_o| - |F_c||)$  $\sum |F_a|$ ) value at this stage for the 2697 reflections was 0.26 for all 33 nonhydrogen atoms included in the structure factor calculation. The nonhydrogen atoms of the structure were subjected to two cycles of isotropic least-squares refinement followed by two cycles of anisotropic refinement. The R value dropped to 0.05. The weighting scheme initially used was based on counting statistics. Each cycle of anisotropic refinement was carried out in two blocks, one for each ion of the structure. All the 29 hydrogen atoms were located by difference Fourier synthesis and were kept fixed with temperature factors of 4.0 Å<sup>2</sup> in the subsequent refinement of the nonhydrogen atoms. Two more cycles of anisotropic least-squares refinement were performed using all 3504 reflections greater than  $1.5\sigma$ . As convergence had not been achieved an error curve  $(|F_o - F_c| versus |F_o|)$  was plotted and the following weighting scheme was found suitable.

$$\frac{1}{\sqrt{w}} = 4.65 \text{ for } |F_{obs}| \le 57.4,$$
$$\frac{1}{\sqrt{w}} = 0.084|F_{obs}| - 0.16 \text{ for } |F_{obs}| > 57.4.$$

Two final anisotropic cycles gave an R value of 0.057 for the 3504 reflections, and 0.062 for all 3990 measured

#### Table 2. Atomic positional and thermal parameters

Positional parameters of non-hydrogen atoms have been multiplied by 10<sup>4</sup> and those of hydrogen atoms, by 10<sup>3</sup>. Anisotropic thermal parameters have been multiplied by 10<sup>4</sup>. The anisotropic temperature factor is of the form exp  $[-(\beta_{11}h^2 + ... + 2\beta_{12}hk + ...)]$ . Standard deviations refer to the least significant digits.

	x	У	Z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
C(1)	-346(2)	971 (2)	2495 (3)	59 (2)	58 (2)	85 (4)	-12 (2)	19 (2)	-1(2)
C(2)	420 (2)	-76(2)	2617 (3)	53 (2)	62 (2)	106 (4)	-11(2)	14 (2)	0 (2)
C(3)	175 (2)	-1119(2)	2499 (4)	63 (2)	58 (2)	125 (5)	-6(2)	16 (2)	4 (3)
C(4)	-880(2)	-1124(2)	2268 (3)	70 (2)	59 (2)	104 (4)	-20(2)	23 (2)	-8(2)
C(5)	-1692(2)	-137(3)	2151 (4)	57 (2)	69 (2)	139 (5)	-20(2)	23 (3)	-8(3)
C(6)	-1396(2)	886 (2)	2280 (4)	55 (2)	57 (2)	130 (5)	-6(2)	25 (2)	-6(3)
C(7)	-1526 (3)	-4747 (3)	4748 (5)	77 (3)	86 (3)	210 (7)	-13(2)	54 (3)	-30(4)
C(8)	-2926 (2)	-2718(3)	5627 (4)	62 (2)	63 (2)	174 (6)	-17 (2)	27 (3)	9 (3)
C(9)	-4087 (3)	-2071 (3)	5475 (4)	62 (2)	66 (2)	203 (6)	-12 (2)	8 (3)	32 (3)
C(10)	- 4802 (4)	-2234 (4)	3776 (6)	100 (3)	96 (3)	263 (9)	-16 (3)	-41 (4)	31 (4)
C(11)	- 4439 (3)	-1372 (3)	6718 (5)	59 (2)	62 (2)	261 (8)	-5 (2)	34 (3)	29 (4)
C(12)	- 5597 (3)	- 744 (4)	6582 (7)	65 (3)	97 (4)	460 (14)	4 (2)	64 (5)	46 (6)
C(13)	- 3744 (3)	-1125 (3)	8378 (5)	97 (3)	81 (3)	231 (8)	- 10 (2)	41 (4)	-2(4)
C(14)	-2557 (2)	- 4839 (2)	7625 (4)	69 (2)	52 (2)	137 (5)	-15 (2)	7 (3)	4 (3)
C(15)	-2443 (3)	-6118 (3)	7291 (5)	95 (3)	53 (2)	213 (7)	-16 (2)	15 (4)	3 (3)
C(16)	-1535 (3)	- 4606 (3)	8713 (5)	79 (3)	92 (3)	173 (6)	-24 (2)	-16 (3)	12 (3)
C(17)	- 3564 (3)	-4238 (3)	8372 (4)	86 (3)	72 (3)	154 (6)	-21 (2)	43 (3)	4 (3)
C(18)	-4623 (3)	-4383 (4)	7305 (6)	75 (3)	121 (4)	273 (9)	- 22 (3)	53 (4)	20 (5)
C(19)	- 3430 (5)	-4621 (5)	10252 (5)	158 (5)	164 (5)	154 (7)	- 49 (4)	60 (5)	15 (5)
N(1)	1576 (2)	- 129 (2)	2947 (4)	55 (2)	80 (2)	179 (5)	-12 (2)	17 (2)	15 (3)
N(2)	-1164 (2)	- 2233 (2)	2153 (3)	85 (2)	72 (2)	122 (4)	- 32 (2)	22 (2)	-3 (2)
N(3)	- 2294 (2)	1922 (2)	2269 (4)	62 (2)	68 (2)	241 (6)	-8(2)	42 (3)	-11 (3)
O(1)	233 (2)	2727 (2)	4051 (3)	106 (2)	85 (2)	175 (4)	- 38 (2)	31 (2)	- 50 (2)
O(2)	- 965 (2)	2983 (2)	1277 (4)	79 (2)	75 (2)	298 (6)	-16(2)	-8 (3)	55 (3)
O(3)	893 (2)	1977 (2)	1473 (3)	79 (2)	81 (2)	154 (4)	-31 (1)	29 (2)	4 (2)
O(4)	2101 (2)	-720 (3)	1969 (4)	74 (2)	127 (3)	375 (8)	-23 (2)	85 (3)	- 66 (4)
O(5)	1933 (2)	389 (2)	4201 (3)	68 (2)	125 (3)	168 (4)	-32 (2)	-16 (2)	11 (3)
O(6)	-2111 (2)	-2201(2)	2012 (3)	91 (2)	98 (2)	220 (5)	-49 (2)	20 (3)	1 (3)
<b>O</b> (7)	- 444 (2)	- 3095 (2)	2202 (3)	109 (2)	55 (2)	198 (5)	- 19 (2)	33 (3)	1 (2)
O(8)	- 2264 (2)	2505 (2)	3572 (4)	106 (3)	96 (3)	336 (7)	-5 (2)	74 (3)	-77 (4)
O(9)	- 3016 (2)	2078 (2)	1036 (4)	67 (2)	104 (3)	314 (7)	9 (2)	6 (3)	14 (3)
S(1)	-11(1)	2312 (1)	2314 (1)	64 (1)	53 (1)	136 (1)	-18(0)	11 (1)	0 (1)
S(2)	– 27 <b>99 (1</b> )	-4261 (1)	5411 (1)	55 (0)	61 (1)	127 (1)	-13 (0)	14 (1)	-3(1)

#### Table 2 (cont.)

	x	у	Ζ	β
H1(C18)	- 522	- 389	780	4∙0
H2(C18)	- 466	-410	611	4∙0
H3(C18)	-461	- 519	726	4∙0
H4(C17)	-356	- 465	941	4∙0
H5(C19)	- 268	- 468	1087	4∙0
H6(C19)	- 395	-407	1084	4'0
H7(C19)	-358	- 541	1019	4∙0
H8(C16)	-133	- 505	980	4·0
H9(C16)	-164	- 377	899	4∙0
H10(C16)	- 93	- 485	806	4·0
H11(C15)	- 291	- 622	615	4∙0
H12(C15)	-167	- 649	720	4∙0
H13(C15)	-264	- 646	821	4∙0
H14(C7)	- 99	-432	547	<b>4</b> ∙0
H15(C7)	- 160	- 457	353	4∙0
H16(C7)	-123	- 558	496	4∙0
H17(C8)	-260	- 246	474	<b>4</b> ∙0
H18(C8)	-250	- 255	681	4∙0
H19(C10)	- 544	-155	350	4∙0
H20(C10)	- 506	- 294	377	4·0
H21(C10)	-438	-232	280	4∙0
H22(C12)	-600	- 80	538	4·0
H23(C12)	- 566	8	690	4∙0
H24(C12)	- 592	- 108	739	4∙0
H25(C13)	- 393	- 147	934	4∙0
H26(C13)	- 391	-26	859	4∙0
H27(C13)	- 298	- 142	835	4∙0
H28(C5)	- 247	-12	198	<b>4</b> ∙0
H29(C3)	76	- 183	258	<b>4</b> ∙0

reflections. The shift/ $\sigma$  ratios for the parameters were all less than one, the average being 0.17. The final standard deviation for an observation of unit weight was 0.78.

Table 1 lists the observed and calculated structure factors. Table 2 lists the positional coordinates and anisotropic temperature factors for the nonhydrogen atoms, and the positional coordinates for the hydrogen atoms. The standard deviations for these parameters have not been corrected to account for the two-part refinement.

Scattering factors used for C, N, O, and S were from Hoerni & Ibers (1954) and that for H was from Stewart, Davidson & Simpson (1965). The full-matrix leastsquares refinement program used was that of Busing, Martin & Levy (1964), modified for the UNIVAC 1108 computer by Rao (1968).

#### **Discussion of results**

The determination of the structure of the final product has made it possible to suggest a reaction mechanism for its formation (scheme 1). In the initial step the episulphonium ion probably reacts with a molecule of 2,3-dimethyl-2-butene to form a three-membered sulphonium ion (1) which then undergoes further reaction with a second molecule of the olefin which involves a hydride shift to generate the cation 2,3-dimethyl-2-butenyl-1,1,2-trimethylpropyl-methyl sulfonium ion (2).

Molecular geometry and conformation of the cation

As expected the sulfonium ion exhibits a pyramidal geometry which is distorted from 3m symmetry in a way predictable from simple steric considerations. First the S–C bonds are found to increase (1.799, 1.830 and 1.882 Å) (Fig. 1) with increasing size of the alkyl group in the order methyl, butenyl, 1,1,2-trimethyl-propyl. Secondly, the increase in the C–S–C angles (101.1, 105.1 and 107.5°) again follows the order of increasing steric interactions between the neighboring alkyl groups (butenyl, methyl>trimethylpropyl, methyl).

In the S-propyl group the C–C bond distances range from 1.519 to 1.564 Å. The significant increase of the C(14)–C(17) bond (1.550  $\pm$  0.005 Å) from the normal paraffinic C-C bond distance (1.533 Å) is also expected from simple steric considerations. But, it is not apparent why the C(17)-C(19) bond is also significantly extended from the normal C-C distance. All of the C-C-



Fig. 1. Atom numbering, bond lengths, bond angles and molecular conformation of 2,3-dimethyl-2-butenyl-1,1,2trimethylpropylmethyl sulfonium ion. The drawings were made with the ORTEP computer program (Johnson, 1965).

 Table 3. Selected torsion angles (°)

The e.s.d.'s in torsion angles are about  $0.4^{\circ}$ .

Sulfonium cation			
C(12)-C(11)-C(9)-C(10)	$-4 \cdot 1$	$C(9)-C(8)-S^{+}-C(7)$	157-0
C(12)-C(11)-C(9)-C(8)	+178.9	$C(8)-S^{+}C(14)-C(17)$	-61.7
C(13)-C(11)-C(9)-C(10)	+175.8	$C(8)-S^{+}C(14)-C(16)$	+ 59.7
C(13)-C(11)-C(9)-C(8)	-1.2	$C(8)-S^{+}C(14)-C(15)$	178.9
$C(11)-C(9)-C(8)-S^+$	-121.6	$S^+ - C(14) - C(17) - C(19)$	<i>−</i> 177·8
$C(9) - C(8) - S^{+} - C(14)$	-93.1	$S^+ - C(14) - C(17) - C(18)$	56.5
2,4,6-Trinitrobenzene sulfo	nate anion (	TNBS)	
O(5) - N(1) - C(2) - C(1)	- 54.3	O(7) - N(2) - C(4) - C(5)	- 177.6
O(5) - N(1) - C(2) - C(3)	123.8	O(6)-N(2)-C(4)-C(3)	-177·27
O(4) - N(1) - C(2) - C(1)	+128.0	O(6)-N(2)-C(4)-C(5)	+ 2.1
O(4) - N(1) - C(2) - C(3)	- 53.9	O(1)-SC(1)C(7)	+ 91.8
O(8) - N(3) - C(6) - C(1)	+61.3	O(1)-SC(1)C(6)	- 97·6
O(8) - N(3) - C(6) - C(5)	-115.5	O(1)-SC(1)C(2)	-147.4
O(9) - N(3) - C(6) - C(1)	-123.2	O(2)-SC(1)C(6)	+ 23 · 1
O(9) - N(3) - C(6) - C(5)	+ 60.0	O(3)-SC(1)C(2)	-28.7
O(7) - N(2) - C(4) - C(3)	+2.9	O(3)-SC(1)C(6)	+ 141.9

C angles in the S-propyl group are significantly greater than the ideal tetrahedral value of 109°28'.

In the S-butenyl group the C–C 'single' bond distances agree with each other within the experimental errors. They range from 1.497 to 1.515 Å, with an average value of 1.506 Å. The angles facing the double bond range from 122.3 to 125.0° with an average value of  $123.4^{\circ}$ , while those opposite the double bond have an average value of 113.6°.

The atoms comprising the ethylenic system show slight but significant deviations from planarity (Fig. 3). Similar lack of planarity of ethylenic systems has also been observed previously (Sundaralingam, 1972). The sulfur atom deviates by 1.49 Å from the ethylene plane, torsion angle C(11)-C(9)-C(8)-S is 121.6°. Single bonds adjacent to double bonds typically show rota-



Fig. 2. Atom numbering, bond lengths, and bond angles of the 2,4,6-trinitrobenzene sulphonate anion.



Fig. 3. Deviations (Å) of the atoms from the least-squares plane of the aromatic ring of the TNBS anion and from the least-squares plane of the ethylene group.

tions of about 120° in a number of other hydrocarbon systems (Marteuscelli, 1969 and references therein; Craven & Cusatis, 1969; Sundaralingam, 1972).

# Molecular geometry and conformation of the TNBS anion

The structure of the trinitrobenzenesulfonate (TNBS) anion (Fig. 2) resembles closely that determined by Meyers & Trueblood (1969). However, the internal consistency of the bond distances of the aromatic ring appears to be much better in the present study. The average C-C bond distance is 1.380 Å, with extreme values of 1.361 and  $1.394 \pm 0.005$  Å, the longer bonds are on the sulfonate side of the ring. This feature together with the observed trends in the internal ring angles are a manifestation of both the steric and electronic properties of the sulfonate and ortho nitro groups extensively discussed by Meyers & Trueblood (1969). In the sulphonate group the S-O bond distances are in excellent agreement with each other, their average value being 1.338 Å. The C-S-O angles are also close to each other and range from 103.0 to 105.1° (average 103.7°), while the O-S-O angles range from 113.9 to  $115.0^{\circ}$  (average  $114.6^{\circ}$ ) and are considerably larger. The forced rotation of the ortho nitro groups by 54 and 61° (Table 3) out of the plane of the benzene ring was also found by Meyers & Trueblood (1969). The *para* nitro group is twisted only  $2.5^{\circ}$  out of the benzene plane compared with 11° found by the latter workers. This difference is attributable to the differences in the intermolecular packing in the two structures (see below).

The deviations of the atoms from the least-squares plane of the benzene ring are shown in Fig. 3. Despite the distortions from planarity of the substituents the benzene ring itself is planar. The sulfonate S atom shows the greatest displacement (0.27 Å) while the nitrogen atoms of the *ortho* nitro groups are displaced 0.07 and 0.10 Å on the opposite sides of it. In contrast the nitrogen atom of the *para* nitro group lies in the plane of the benzene ring. Apparently the amount of displacement of the nitrogen atoms from the benzene plane is related to the degree of twist of the nitro groups.

#### Crystal packing and interionic contacts

The negative charge on the trinitrobenzenesulfonate anion is expected to be more delocalized than the positive charge on the sulfonium ion which is certainly stabilized by induction from the three alkyl groups. The closest contact of  $3 \cdot 309$  Å between the oppositely charged ions involves the methyl carbon atom C(7) of the sulfonium ion and the sulfonate oxygen atom O(1) (Fig. 4). Considerably shorter contacts are observed between the TNBS ions, the shortest being 2.963 Å, involving O(1) of the sulphonate and O(7) of the *para* nitro group of a symmetry-related ion. The latter contact is primarily responsible for keeping the *para* nitro groups close to the benzene plane. Adjacent benzene rings are held 3.95 to 4.01 Å apart by the sulphonate group and rotated *ortho* nitro groups. Intermolecular distances less than 3.4 Å are shown in Fig. 4.

We wish to thank Drs G. Helmkamp and E. Carbin for supplying the crystals of the compound, and Dr R. K. McMullan for helpful discussions. This work was supported by a research grant GP 15977 from the National Science Foundation and in part by a grant of computer time by the Wisconsin Alumni Research Foundation.

#### References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). ORFLS. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- CARBIN, E. & HELMKAMP, G. K. (1970). Private communication.
- CARBIN, E., HELMKAMP, G. K., BARNES, W. M. & SUNDARA-LINGAM, M. (1972). Int. J. Sulfur Chem. 2, 129–132.
- CRAVEN, B. M. & CUSATIS, C. (1969). Acta Cryst. B25, 2291-2298.
- HOERNI, J. A. & IBERS, J. (1954). Acta Cryst. 7, 744-746.

JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

MARTEUSCELLI, E. (1969). Acta Cryst. B25, 2540-2546.



Fig. 4. A view along an arbitrary direction showing the arrangement of the ions and the intermolecular contacts less than 3.4 Å.

MEYERS, M. & TRUEBLOOD, K. N. (1969). Acta Cryst. B25, 2588–2598. PETTIT, D. J. & HELMKAMP, G. K. (1963). J. Org. Chem. 28.

2932–2933. Реттіт, D. J. & Helmkamp, G. K. (1964). J. Org. Chem. 29,

2702–2706. RAO, S. T. (1968). Unpublished work. STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). J. Chem. Phys. 42, 3175–3187.

STOUT, G. H. & JENSEN, L. H. (1968). X-ray Structure Determination. New York: Macmillan.

SUNDARALINGAM, M. (1972). Ann. N. Y. Acad. Sci. 195, 324–355.

WILSON, A. J. C. (1942). Nature, Lond. 150, 151-152.

#### Acta Cryst. (1973). B29, 1875

# The Crystal and Molecular Structure of Dimethyl trans, trans-2,5-Dichloromuconate

BY HOWARD EINSPAHR\*

A. A. Noyes Laboratories of Chemical Physics, California Institute of Technology,<sup>†</sup> Pasadena, California 91109, U.S.A.

#### AND JERRY DONOHUE

Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104, U.S.A.

#### (Received 29 January 1973; accepted 5 March 1973)

The structure of dimethyl *trans, trans*-2,5-dichloromuconate,  $C_8H_8O_4Cl_2$ , was determined by singlecrystal X-ray diffraction techniques. The unit cell is monoclinic, space group  $P2_1/n$ , with the following dimensions at  $23 \pm 2^{\circ}C$ : a = 3.967 (1), b = 23.339 (5), c = 5.483 (1) Å,  $\beta = 95.80$  (1)°. There are two molecules in the unit cell; the molecules lie on centers of symmetry. The data were collected on an automated diffractometer. The structure was refined by full-matrix least-squares; the final value of the conventional R index is 0.041. The molecules lie in densely packed layers parallel to (101). The carbonyl oxygen assumes the antiplanar conformation with respect to the  $\beta$ -carbon atom. Nonbonded intramolecular distances do not show a significant preference for one conformer over the other.

## Introduction

The conformation of the carboxyl group, a representation of which is shown in Fig. 1, has been a subject of interest in a number of laboratories over the past few years. The preferred conformation at the carboncarbon bond has been found to be the one which places the  $\alpha$ ,  $\beta$  carbon-carbon bond synplanar to the carbonyl (Leiserowitz & Schmidt, 1965). This preference is attributed by Leiserowitz and Schmidt to nonbonded interactions between the  $\beta$ -carbon and its hydrogen atoms, on the one hand, and the hydroxyl or carbonyl oxygen atoms, on the other. Chiefly due to the difference in carbon-carbon-carbonyl oxygen and -hydroxyl oxygen angles (characteristically about 122 and 114°, respectively), nonbonded  $\beta$ -carbon-oxygen and hydrogen-oxygen distances are 0.1 and 0.2 Å greater in the synplanar than in the antiplanar conformers.

This preference in conformation is amply confirmed for saturated acids, which are synplanar with only a few exceptions. However, the extension of this con-

A C 29B - 9

formation to  $\alpha$ , $\beta$ -unsaturated acids on the basis of the same nonbonded interaction arguments is less satisfactory. Table 1 contains a list of  $\alpha$ , $\beta$ -unsaturated acids and esters whose structures are known, together with the respective conformations about the carboxyl carbon-carbon bond. Of the twenty-three crystallographically independent carboxyl groups represented in this table, nine are known to be antiplanar.

As Dunitz & Strickler (1968) point out, nonbonded interactions cannot be the sole factor determining conformations at the carbon-carbon bond in these compounds. They suggest that the bent-bond description of double bonds may be useful as a model of the interactions which produce the antiplanar conformation. If the carbonyl double bond is considered as two bent single bonds, then staggering about C-C $\alpha$  in saturated acids leads to the synplanar conformation. However, in  $\alpha$ , $\beta$ -unsaturated acids, with two double bonds to be resolved into bent bonds, staggering about C-C $\alpha$  gives the antiplanar conformation. In the latter case, the preference for the staggered conformation is in opposition to the steric factor and admits the possibility of antiplanar conformations.

While the bent-bond concept does rationalize the appearance of antiplanar conformations in unsaturated acids, it does not enable one to predict the conformations in such acids whose structures are not known.

<sup>\*</sup> Present address: Institute of Dental Research and Department of Biochemistry, University of Alabama in Birmingham, 1919 Seventh Avenue South, Birmingham, Alabama 35233, U.S.A.

<sup>†</sup> Contribution No. 4606 from the Arthur Amos Noyes Laboratory of Chemical Physics.