# The Structure of a Carbonium Ion. Refinement of the Crystal and Molecular Structure of *sym*-Triphenylcyclopropenium Perchlorate

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**Abstract:** *sym*-Triphenylcyclopropenium cation was the first $2\pi$-electron aromatic system to be synthesized. Crystals of the salt *sym*-triphenylcyclopropenium perchlorate, $C_{21}H_{15}ClO_4$, are monoclinic, space group $P2_1/c$. Unit cell constants measured with a diffractometer are: $a = 9.960 \pm 0.001$, $b = 12.069 \pm 0.003$, $c = 17.285 \pm 0.004$, and $\beta = 120° 50' \pm 2'$ (Cu K$\alpha$ = 1.5418 Å.). The structure has been refined by the full-matrix least-squares method to an $R$ factor of 7.5% using integrated photometric data. The triphenylcyclopropenium cation is nonplanar, and the phenyl groups are twisted in a propeller-like arrangement making angles of 7.6, 12.1, and 21.2° with respect to the cyclopropenium plane. While the latter plane and the three atoms attached to it lie approximately in a plane, the three atoms at the farthermost points of the system are significantly displaced on the same side of this plane. The average C–C bond length of the cyclopropenium ring is $1.373 \pm 0.005$ Å., appreciably shorter than the benzene C–C bond, and is the first reported value for a C–C bond in a $2\pi$-electron aromatic system. The average exocyclic single bond length of 1.436 Å. is considerably less than the normal C($sp^2$)–C($sp^2$) single bond. The thermal vibration of the phenyl groups is quite large and the perchlorate ion executes a large librational motion. The structure consists of triphenylcyclopropenium ions and perchlorate ions disposed in a zigzag arrangement along the $b$ axis. The cations are sandwiched between the anions while the anions (nuts) are held by pairs of cations (nutcrackers). The shortest intermolecular contacts in the structure are between the oxygens of the perchlorate and the formally positive carbons of the cyclopropenium ring.

The Hückel $(4n + 2)\pi$-electron rule of aromatic stability predicts a stable cyclopropenium cation, but thus far this species has not been isolated. This simple system and its derivatives are of considerable interest to the theoretical chemists. The *sym*-triphenylcyclopropenium (TPCP$^+$) carbonium ion was the first derivative to be prepared.[2] A preliminary note on the solution of the crystal structure of *sym*-triphenylcyclopropenium perchlorate based on visually estimated X-ray diffraction data has been published.[3] We report here the refinement of the structure based on integrated photometric data.

Other carbonium ions whose structures have been determined by the method of X-ray diffraction techniques are: triphenylmethyl perchlorate,[4] *p*-rosaniline perchlorate,[5] and 3-chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate.[6]

## Experimental Section

A generous supply of the compound was provided by Professor Ronald Breslow of Columbia University. Suitable crystals for the present investigation were crystallized from solutions of acetonitrile dried over phosphorus pentoxide. The needle-like crystals are monoclinic and are elongated along the $b$ axis. Unit cell constants measured on a diffractometer are: $a = 9.960 \pm 0.001$, $b = 12.069 \pm 0.003$, $c = 17.285 \pm 0.004$ Å., and $\beta = 120° 50' \pm 2'$ (Cu K$\alpha$ = 1.5418 Å.). The space group is $P2_1/c$ with four molecules of $C_{21}H_{15}ClO_4$ per unit cell.

Unidimensionally integrated equi-inclination Weissenberg photographs were taken for the levels $h0l$ to $h11l$ and $hk0$ to $hk2$ from two different crystals. The direction of integration by the camera was at right angles to the translation of the film. These were scanned at right angles to the direction of integration by a recording microdensitometer having a logarithmic response. The areas above background of the peaks on the recorder tracings are proportional to the integrated intensities. After applying the usual corrections to the intensities, the $b$-axis data were put on a common scale using the $c$-axis data for determining the interlevel scale factor. A total of 1618 independent reflections, ranging in $\sin \theta/\lambda$ from 0.0581 to 0.6441 and comprising about 73% of the data accessible with Cu K$\alpha$ radiation, were observed. The minimum observed structure amplitude was 2.7.

The structure was solved from the Patterson–Harker section at $y = 1/2$ and considerations of packing and a few low-order reflections.[3] The structure refined to an $R$ of 13% using the original visually estimated data. This rather high value was undoubtedly due to the quality of the data and the large thermal vibrations of some of the atoms in the structure. To improve on the precision of the atomic coordinates, we collected the present integrated data. The beginning coordinates for the full-matrix least-squares refinement were those from the visually estimated data. A modified Hughes[7] weighting scheme was used: $\sqrt{w} = 1.0$ if $F_0 \leq 20$; $\sqrt{w} = 20/F_0$ if $F_0 > 20$. Initially, the hydrogen atoms were fixed at calculated positions, 1.0 Å. from the atoms to which they were attached. Since there are 26 nonhydrogen atoms, the anisotropic refinement was carried out in two parts such that the cyclopropenium ring atoms were common to both the parts. After three complete least-squares cycles of the nonhydrogen atoms, they were fixed, and the hydrogen atom positional and isotropic temperature factors were refined. A second round of least-squares cycles on the nonhydrogens (hydrogen, fixed) and hydrogens (nonhydrogen, fixed) completed the refinement. The $R$ factor for the observed reflections, excluding 14 which suffered secondary extinction, is 7.5%. A $\Delta F$ map, based on $F_c$ calculated with only the nonhydrogen atom contributions, gave all the hydrogen electron densities unequivocally (Figure 1).

The scattering factors of C, O, and Cl were those of the neutral species,[8a] and that of H was from Stewart, Davidson, and Simpson.[8b]

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[1] Children's Cancer Research Foundation, Children's Hospital Medical Center, and Harvard Medical School, Boston, Mass.

[2] R. Breslow and C. Yuan, *J. Am. Chem. Soc.*, **80**, 5991 (1958).

[3] M. Sundaralingam and L. H. Jensen, *ibid.*, **85**, 3302 (1963).

[4] A. H. Gomes de Mesquita, C. H. MacGillavry, and K. Eriks, *Acta Cryst.*, **18**, 437 (1965).

[5] K. Eriks and L. L. Koh, Program and Abstracts, American Crystallographic Association Meetings, Massachusetts Institute of Technology, Cambridge, Mass., March 28–30, 1963.

[6] R. F. Bryan, *J. Am. Chem. Soc.*, **86**, 733 (1964).

[7] E. W. Hughes, *ibid.*, **63**, 1737 (1941).

[8] (a) "International Tables for X-ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, p. 202; (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3178 (1965).

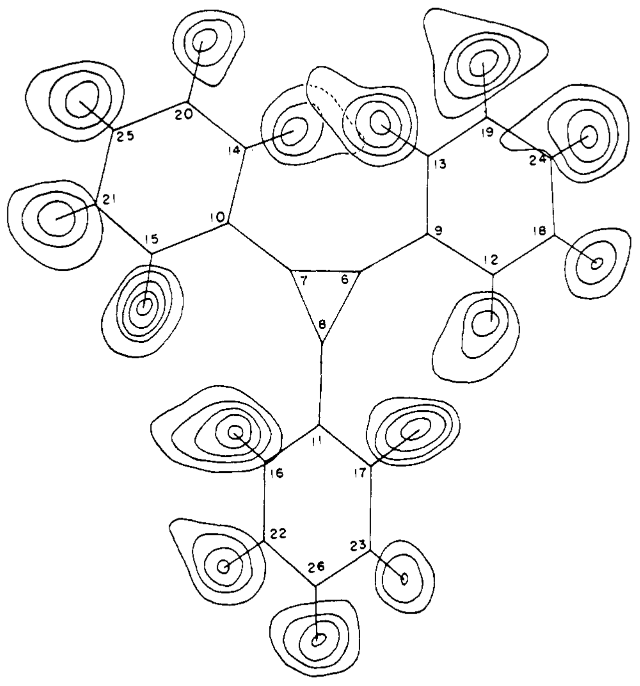

Figure 1. Composite difference Fourier showing hydrogen electron densities. Contours at intervals of 0.1 electron/Å.$^3$, beginning at 0.1 electron/Å.$^3$.

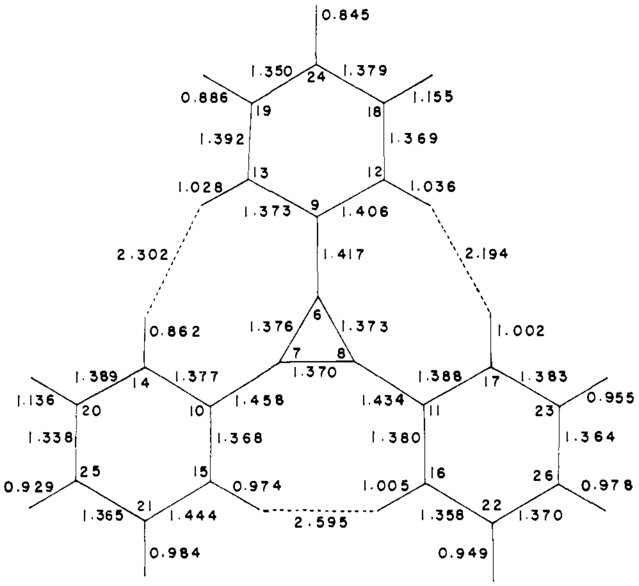

Figure 2. Bond lengths in the triphenylcyclopropenium cation.

## Discussion

The atomic parameters together with their e.s.d.'s (estimated standard deviations) are listed in Tables I, II, and III. A list of the observed and calculated structure amplitudes has been deposited with the American Documentary Institute. As would be expected, the atoms farther removed from the centroid of the molecule possess larger thermal parameters and consequently have higher standard deviations. The average e.s.d.'s (in Å.) of the atomic positions are: Cl = $0.001_6$, O = $0.008_7$, C (cyclopropenium) = $0.006_6$, C (phenyl) = $0.008_3$, and H = $0.07_1$.

With the revised scattering factors for hydrogen it is observed that the majority of the hydrogen atom temperature factors are greater than the carbon atoms to which they are attached (Table III).[9] However, on the contrary, McWeeny's[10] scattering factors for hydrogen yielded hydrogen atom temperature factors which were in general lower.[11,12]

The bond lengths and bond angles uncorrected for thermal oscillations are shown in Figure 2 and Tables IV and V. The average C($sp^2$)-H bond length of 0.981 Å. is in good agreement with the values obtained from X-ray studies of several other compounds.[8]

The cyclopropenium ring is indeed symmetrical and the three C–C bonds are in remarkable agreement with each other. A striking feature is that their average value of 1.373 ± 0.005 Å. is significantly shorter than the C–C bond in benzene.[13] It should be noted that for the cyclopropenium C–C bond, corrections for rotational oscillation effects would be small.[14] The shortening may be explained as due to the attractive force between the formally positive carbon of the cyclopropenium ring, and the p$\pi$ electrons opposite to them,

Table I. Positional Coordinates and Their Estimated Standard Deviations[a]

| | $x/a$ ($\sigma$) | $y/b$ ($\sigma$) | $z/c$ ($\sigma$) |
|---|---|---|---|
| Cl | 2300 (2) | 2519 (1) | 2643 (1) |
| O-2 | 2687 (14) | 3282 (7) | 2247 (7) |
| O-3 | 2827 (7) | 1447 (4) | 2615 (4) |
| O-4 | 2568 (10) | 2821 (6) | 3476 (4) |
| O-5 | 0618 (8) | 2468 (7) | 2142 (7) |
| C-6 | 0872 (7) | 5242 (4) | 2806 (4) |
| C-7 | −0204 (7) | 4669 (4) | 2924 (4) |
| C-8 | −0528 (8) | 4923 (5) | 2073 (5) |
| C-9 | 2350 (7) | 5766 (4) | 3191 (4) |
| C-10 | −0609 (8) | 4151 (4) | 3540 (4) |
| C-11 | −1560 (7) | 4866 (5) | 1115 (4) |
| C-12 | 2908 (8) | 6142 (6) | 2637 (5) |
| C-13 | 3254 (9) | 5907 (6) | 4108 (5) |
| C-14 | 0565 (9) | 3891 (6) | 4401 (5) |
| C-15 | −2144 (10) | 3953 (6) | 3261 (5) |
| C-16 | −2848 (9) | 4177 (5) | 0748 (5) |
| C-17 | −1262 (9) | 5508 (6) | 0554 (5) |
| C-18 | 4342 (10) | 6641 (7) | 3012 (7) |
| C-19 | 4708 (10) | 6417 (7) | 4474 (6) |
| C-20 | 0199 (12) | 3378 (7) | 4989 (5) |
| C-21 | −2491 (10) | 3439 (7) | 3892 (6) |
| C-22 | −3832 (9) | 4113 (6) | −0158 (5) |
| C-23 | −2273 (11) | 5449 (7) | −0368 (6) |
| C-24 | 5227 (9) | 6776 (7) | 3933 (8) |
| C-25 | −1290 (13) | 3152 (6) | 4727 (6) |
| C-26 | −3526 (10) | 4751 (8) | −0705 (5) |
| H-27 | 2137 (81) | 6004 (60) | 1957 (49) |
| H-28 | 4810 (82) | 6971 (63) | 2567 (46) |
| H-29 | 6072 (74) | 7139 (52) | 4188 (42) |
| H-30 | 5171 (62) | 6555 (47) | 5058 (38) |
| H-31 | 2883 (71) | 5540 (51) | 4503 (39) |
| H-32 | 1523 (83) | 4033 (57) | 4563 (46) |
| H-33 | 1260 (90) | 3201 (69) | 5678 (53) |
| H-34 | −1468 (76) | 2733 (54) | 5116 (44) |
| H-35 | −3590 (71) | 3417 (51) | 3735 (41) |
| H-36 | −3016 (58) | 4151 (40) | 2668 (32) |
| H-37 | −3062 (66) | 3762 (49) | 1177 (37) |
| H-38 | −4696 (76) | 3625 (56) | −0363 (43) |
| H-39 | −4204 (82) | 4811 (57) | −1359 (47) |
| H 40 | −2208 (79) | 5966 (56) | −0765 (44) |
| H-41 | −0338 (64) | 6009 (45) | 0892 (36) |

[a] E.s.d.'s, $\sigma$, in parentheses, all multiplied by $10^4$.

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(9) L. H. Jensen, Program and Abstracts, American Crystallographic Association Meetings, Suffern, N. Y., 1965, p. 12.

(10) R. McWeeny, *Acta Cryst.*, **4**, 513 (1951).

(11) M. Sundaralingam and L. H. Jensen, *ibid.*, **16**, A61 (1963).

(12) L. H. Jensen and M. Sundaralingam, *Science*, **145**, 1185 (1964).

(13) D. W. J. Cruickshank, *Acta Cryst.*, **2**, 65 (1949).

(14) D. W. J. Cruickshank, *ibid.*, **9**, 757 (1956).

**Table II.** Anisotropic Thermal Parameters and Their Estimated Standard Deviations[a]

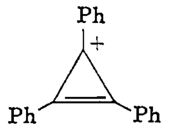
| | $b_{11} \times 10^4$ | $b_{22} \times 10^4$ | $b_{33} \times 10^4$ | $b_{12} \times 10^4$ | $b_{13} \times 10^4$ | $b_{23} \times 10^4$ |
|---|---|---|---|---|---|---|
| Cl | 0147 (1) | 0057 (5) | 0037 (3) | 0010 (8) | 0036 (5) | −0001 (4) |
| O-2 | 1028 (18) | 0114 (4) | 0255 (5) | 0020 (6) | 0413 (9) | 0047 (3) |
| O-3 | 0274 (5) | 0070 (2) | 0116 (2) | 0016 (3) | 0111 (3) | −0008 (2) |
| O-4 | 0656 (12) | 0203 (4) | 0068 (2) | 0129 (6) | 0128 (4) | −0001 (2) |
| O-5 | 0235 (7) | 0169 (4) | 0204 (4) | 0036 (4) | 0030 (4) | −0043 (3) |
| C-6 | 0150 (6) | 0046 (2) | 0048 (2) | 0002 (3) | 0052 (3) | 0003 (1) |
| C-7 | 0156 (5) | 0047 (2) | 0046 (2) | 0012 (3) | 0050 (2) | 0005 (1) |
| C-8 | 0157 (6) | 0047 (2) | 0055 (2) | −0004 (3) | 0059 (3) | 0002 (1) |
| C-9 | 0158 (5) | 0057 (2) | 0044 (2) | −0009 (3) | 0044 (2) | −0002 (1) |
| C-10 | 0167 (6) | 0056 (2) | 0053 (2) | −0003 (3) | 0064 (3) | −0002 (1) |
| C-11 | 0152 (6) | 0056 (2) | 0049 (2) | 0008 (3) | 0045 (2) | 0002 (1) |
| C-12 | 0157 (6) | 0109 (3) | 0056 (2) | −0015 (3) | 0045 (3) | 0006 (2) |
| C-13 | 0195 (7) | 0076 (3) | 0063 (2) | −0002 (3) | 0057 (3) | −0004 (2) |
| C-14 | 0198 (7) | 0092 (3) | 0062 (2) | 0027 (3) | 0070 (3) | 0021 (2) |
| C-15 | 0227 (8) | 0102 (3) | 0051 (2) | −0037 (4) | 0056 (3) | −0004 (2) |
| C-16 | 0190 (6) | 0075 (3) | 0056 (2) | −0002 (3) | 0057 (3) | −0006 (2) |
| C-17 | 0193 (7) | 0079 (3) | 0058 (2) | 0006 (3) | 0048 (3) | 0009 (2) |
| C-18 | 0182 (8) | 0126 (4) | 0102 (3) | −0029 (4) | 0075 (4) | 0023 (3) |
| C-19 | 0172 (7) | 0094 (3) | 0075 (3) | −0004 (4) | 0018 (4) | −0016 (2) |
| C-20 | 0323 (10) | 0107 (4) | 0059 (2) | 0038 (5) | 0095 (4) | 0022 (2) |
| C-21 | 0228 (8) | 0126 (4) | 0087 (3) | −0059 (4) | 0099 (4) | −0016 (3) |
| C-22 | 0206 (7) | 0100 (3) | 0055 (2) | −0009 (4) | 0040 (3) | −0017 (2) |
| C-23 | 0284 (9) | 0106 (4) | 0064 (2) | 0042 (5) | 0080 (4) | 0025 (2) |
| C-24 | 0131 (6) | 0085 (3) | 0119 (4) | −0012 (4) | 0040 (4) | 0013 (3) |
| C-25 | 0355 (11) | 0081 (3) | 0082 (3) | −0016 (5) | 0127 (5) | 0003 (2) |
| C-26 | 0203 (8) | 0126 (4) | 0047 (2) | 0047 (4) | 0025 (3) | −0006 (2) |

[a] E.s.d.'s in parentheses. The $b_{ij}$'s are defined by the expression $T = \exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})]$.

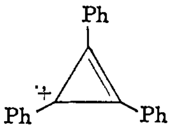
**Table III.** Comparison of the Isotropic Temperature Factor of the Hydrogen Atoms and the Carbon Atoms to Which They Are Attached

| | $B_C$, Å.$^2$ | | $B_H$, Å.$^2$ | $\Delta B = B_H - B_C$, Å. |
|---|---|---|---|---|
| C-12 | 5.1 | H-27 | 7.8 | 2.7 |
| C-13 | 4.7 | H-31 | 5.5 | 0.8 |
| C-14 | 4.7 | H-32 | 7.7 | 3.0 |
| C-15 | 5.0 | H-36 | 3.3 | −1.7 |
| C-16 | 4.3 | H-37 | 5.2 | 0.9 |
| C-17 | 4.5 | H-41 | 4.7 | 0.2 |
| C-18 | 5.8 | H-28 | 8.2 | 2.4 |
| C-19 | 5.0 | H-30 | 4.7 | −0.3 |
| C-20 | 5.1 | H-33 | 9.3 | 4.2 |
| C-21 | 5.7 | H-35 | 6.1 | 0.4 |
| C-22 | 5.3 | H-38 | 6.8 | 1.5 |
| C-23 | 5.4 | H-40 | 6.9 | 1.5 |
| C-24 | 5.8 | H-29 | 6.2 | 0.4 |
| C-25 | 5.6 | H-34 | 6.5 | 0.9 |
| C-26 | 5.6 | H-39 | 7.1 | 1.5 |

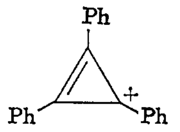
in the valence-bond structures I, II, and III. Furthermore, one might invoke the concept of the "bent"



I



II



III

bonds or "banana" bonds[15] as proposed for cyclopropane to apply to the σ skeleton of the cyclopropenium ring.

The Hückel molecular orbital calculation for the planar *sym*-triphenylcyclopropenium cation gives a bond order of 0.576, which corresponds to a C–C bond length of 1.409 Å., for the three-membered ring (column 2, Table VI). This may be compared with the shorter value, 1.390 Å. (bond order 0.677),[16] obtained for the parent cyclopropenyl cation. The calculated bond lengths for the remaining C–C bonds are shown in Table VI. Calculations were also performed, taking into account the tilt of the phenyl groups, where $\beta^\theta$

**Table IV.** Bond Lengths[a] (Å.)

| | | | |
|---|---|---|---|
| Cl–O-2 | 1.318 | C-12–H-27 | 1.036 |
| Cl–O-3 | 1.406 | C-13–H-31 | 1.028 |
| Cl–O-4 | 1.372 | C-14–H-32 | 0.862 |
| Cl–O-5 | 1.439 | C-15–H-36 | 0.974 |
| C-6–C-7 | 1.376 | C-16–H-37 | 1.005 |
| C-6–C-8 | 1.373 | C-17–H-41 | 1.002 |
| C-7–C-8 | 1.370 | C-18–H-28 | 1.155 |
| C-6–C-9 | 1.417 | C-19–H-30 | 0.886 |
| C-7–C-10 | 1.458 | C-20–H-33 | 1.136 |
| C-8–C-11 | 1.434 | C-21–H-35 | 0.984 |
| C-9–C-12 | 1.406 | C-22–H-38 | 0.949 |
| C-9–C-13 | 1.373 | C-23–H-40 | 0.955 |
| C-10–C-14 | 1.379 | C-24–H-29 | 0.845 |
| C-10–C-15 | 1.368 | C-25–H-34 | 0.929 |
| C-11–C-16 | 1.380 | C-26–H-39 | 0.978 |
| C-11–C-17 | 1.388 | | |
| C-12–C-18 | 1.369 | | |
| C-13–C-19 | 1.392 | | |
| C-14–C-20 | 1.389 | | |
| C-15–C-21 | 1.444 | | |
| C-16–C-22 | 1.358 | | |
| C-17–C-23 | 1.383 | | |
| C-18–C-24 | 1.379 | | |
| C-19–C-24 | 1.350 | | |
| C-20–C-25 | 1.338 | | |
| C-21–C-25 | 1.365 | | |
| C-22–C-26 | 1.370 | | |
| C-23–C-26 | 1.364 | | |

[a] Approximate standard deviations in the individual bonds, for example, σ (A–B), can be obtained from the expression $\sigma(\text{A–B}) = (\sigma(\text{A})^2 + \sigma(\text{B})^2)^{1/2}$ where σ(A) and σ(B) are the average standard deviations, Table I, in the positions of atoms A and B, respectively.[13]

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(15) C. A. Coulson, "Valence," Oxford University Press, Amen House, London, 1952.

(16) A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961.

**Table V.** Bond Angles[a]

| Bond | ∠, deg. | Bond | ∠, deg. |
|---|---|---|---|
| O-2–Cl–O-3 | 114.25 | C-9–C-12–H-27 | 113.51 |
| O-2–Cl–O-4 | 114.09 | C-18–C-12–H-27 | 126.48 |
| O-2–Cl–O-5 | 106.06 | C-9–C-13–H-31 | 117.81 |
| O-3–Cl–O-4 | 113.96 | C-19–C-13–H-31 | 122.20 |
| O-3–Cl–O-5 | 106.27 | C-10–C-14–H-32 | 119.35 |
| O-4–Cl–O-5 | 100.59 | C-20–C-14–H-32 | 120.88 |
| C-7–C-6–C-8 | 59.78 | C-10–C-15–H-36 | 124.17 |
| C-7–C-6–C-9 | 148.80 | C-21–C-15–H-36 | 118.07 |
| C-8–C-6–C-9 | 151.42 | C-11–C-16–H-37 | 117.38 |
| C-6–C-7–C-8 | 60.01 | C-22–C-16–H-37 | 121.44 |
| C-6–C-7–C-10 | 148.42 | C-11–C-17–H-41 | 113.08 |
| C-8–C-7–C-10 | 151.53 | C-23–C-17–H-41 | 127.72 |
| C-6–C-8–C-7 | 60.21 | C-12–C-18–H-28 | 121.05 |
| C-6–C-8–C-11 | 150.05 | C-24–C-18–H-28 | 119.42 |
| C-7–C-8–C-11 | 149.72 | C-13–C-19–H-30 | 114.42 |
| C-6–C-9–C-12 | 120.10 | C-24–C-19–H-30 | 124.74 |
| C-6–C-9–C-13 | 120.44 | C-14–C-20–H-33 | 113.54 |
| C-12–C-9–C-13 | 119.46 | C-25–C-20–H-33 | 126.14 |
| C-7–C-10–C-14 | 119.16 | C-15–C-21–H-35 | 117.79 |
| C-7–C-10–C-15 | 119.61 | C-25–C-21–H-35 | 122.26 |
| C-14–C-10–C-15 | 121.21 | C-16–C-22–H-38 | 116.61 |
| C-8–C-11–C-16 | 120.48 | C-26–C-22–H-38 | 124.77 |
| C-8–C-11–C-17 | 119.74 | C-17–C-23–H-40 | 121.17 |
| C-16–C-11–C-17 | 119.78 | C-26–C-23–H-40 | 118.70 |
| C-9–C-12–C-18 | 120.01 | C-18–C-24–H-29 | 122.68 |
| C-9–C-13–C-19 | 119.54 | C-19–C-24-H-29 | 115.96 |
| C-10–C-14–C-20 | 119.75 | C-20–C-25–H-34 | 117.15 |
| C-10–C-15–C-21 | 117.75 | C-21–C-25–H-34 | 120.96 |
| C-11–C-16–C-22 | 121.08 | C-22–C-26–H-39 | 125.02 |
| C-11–C-17–C-23 | 119.06 | C-23–C-26–H-39 | 112.74 |
| C-12–C-18–C-24 | 119.52 | | |
| C-13–C-19–C-24 | 120.38 | | |
| C-14–C-20–C-25 | 120.30 | | |
| C-15–C-21–C-25 | 119.25 | | |
| C-16–C-22–C-26 | 118.62 | | |
| C-17–C-23–C-26 | 119.41 | | |
| C-18–C-24–C-19 | 121.10 | | |
| C-20–C-25–C-21 | 121.66 | | |
| C-22–C-26–C-23 | 122.04 | | |

[a] Average e.s.d.'s in bond angles are: O–Cl–O = 0.4°, C–C–C = 0.6°, and C–C–H = 3°.

**Table VI.** Calculated Bond Orders (in Parentheses) and Bond Lengths (Å.)[a]

| C–C bond | I[b] | II[c] | III[d] |
|---|---|---|---|
| 6–7 | 1.409 (0.576) | 1.408 (0.582) | 1.405 (0.588) |
| 6–8 | 1.409 (0.576) | 1.409 (0.577) | 1.409 (0.578) |
| 7–8 | 1.409 (0.576) | 1.407 (0.584) | 1.404 (0.592) |
| 6–9 | 1.450 (0.391) | 1.451 (0.387) | 1.452 (0.383) |
| 7–10 | 1.450 (0.391) | 1.457 (0.368) | 1.462 (0.345) |
| 8–11 | 1.450 (0.391) | 1.452 (0.383) | 1.455 (0.374) |
| 9–12 | 1.402 (0.611) | 1.402 (0.613) | 1.401 (0.614) |
| 9–13 | 1.402 (0.611) | 1.402 (0.613) | 1.401 (0.614) |
| 10–14 | 1.402 (0.611) | 1.400 (0.618) | 1.399 (0.624) |
| 10–15 | 1.402 (0.611) | 1.400 (0.618) | 1.399 (0.624) |
| 11–16 | 1.402 (0.611) | 1.401 (0.614) | 1.401 (0.616) |
| 11–17 | 1.402 (0.611) | 1.401 (0.614) | 1.401 (0.616) |
| 12–18 | 1.389 (0.679) | 1.389 (0.678) | 1.389 (0.678) |
| 13–19 | 1.389 (0.679) | 1.389 (0.678) | 1.389 (0.678) |
| 14–20 | 1.389 (0.679) | 1.390 (0.677) | 1.390 (0.676) |
| 15–21 | 1.389 (0.679) | 1.390 (0.677) | 1.390 (0.676) |
| 16–22 | 1.389 (0.679) | 1.389 (0.678) | 1.390 (0.677) |
| 17–23 | 1.389 (0.679) | 1.389 (0.678) | 1.390 (0.677) |
| 18–24 | 1.393 (0.658) | 1.393 (0.659) | 1.393 (0.659) |
| 19–24 | 1.393 (0.658) | 1.393 (0.659) | 1.393 (0.659) |
| 20–25 | 1.393 (0.658) | 1.393 (0.659) | 1.393 (0.660) |
| 21–25 | 1.393 (0.658) | 1.393 (0.659) | 1.393 (0.660) |
| 22–26 | 1.393 (0.658) | 1.393 (0.659) | 1.393 (0.659) |
| 23–26 | 1.393 (0.658) | 1.393 (0.659) | 1.393 (0.659) |

[a] The bond orders were converted into bond lengths using the bond order–bond length correlation curve of R. Daudel, R. Lefebvre, and C. M. Moser, "Quantum Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959. [b] All $\alpha$'s equal, and all $\beta$'s equal; planar cation assumed. [c] All $\alpha$'s equal, and $\beta^{\theta} \propto \cos \theta$. [d] All $\alpha$'s equal, and $\beta^{\theta} \propto \cos^2 \theta$.

was assumed to be proportional to $\cos \theta$ and $\cos^2 \theta$[17,18] (columns 3 and 4, respectively, Table VI). It should be noted that the calculated values for the C–C bonds of the $2\pi$-electron aromatic system in TPCP$^+$ are about 0.03 Å. greater than the experimental values. This may be attributed to neglect of (a) variations in the Coulomb integral ($\alpha$) and (b) strain in the three-membered ring.

The C–C bond lengths of the phenyl groups show a wide scatter, ranging from 1.338 to 1.444 Å., with an average of 1.377 Å. The extreme values belong to the same phenyl group. The marked variations in the C–C bonds are attributed to the large thermal motion of the phenyl groups and possibly due to feed-back effects arising from the large libration of the perchlorate group. The high-temperature factor of the crystal has imposed severe limitation on the precision of the structure determination, even though extreme care was taken in the intensity measurements. Fortunately, however, the most important structural parameter, the cyclopropenium C–C bond, was obtained with reasonable precision.

The average exocyclic C–C bond length of 1.436 Å. is considerably shorter than the "normal" C(sp$^2$)–C(sp$^2$) single bond length of 1.48 Å.[19,20] This shortening may be ascribed in part to the enhanced conjugation of the phenyl groups to the positively charged cyclopropenium ring, but it is more likely due to the large exocyclic angle, about 150°, around the carbons (C-6, C-7, and C-8) which confer on the orbitals (pointing toward the phenyl groups) of these atoms an amount of s character greater than that of the usual sp$^2$-hybridized orbital. Hence, the hybridization here may be said to be between that of an sp$^2$ (120°) and sp (180°) orbital. This would account for the observed shortening of the exocyclic bond. Similar explanations may be given to the short C(sp$^2$)–C(sp$^2$) single bonds reported in 1-cyclohexenyl-1-cyclobutene (1.436 Å.[21]) and 1,2,3,4-tetraphenylcyclobutenium pentachlorostannate (1.41 Å.).[6]

In theoretical calculations the *sym*-triphenylcyclopropenium cation has been assumed planar.[22,23] This investigation reveals the fact that the system is nonplanar and the phenyl rings are twisted in a propeller-like arrangement. The phenyl rings on C-6, C-8, and C-7 make angles of 7.6, 12.1, and 21.2°, respectively, to the plane of the three-membered ring. It may be fortuitous that the exocyclic C–C bond lengths increase with increase in this twist angle, but it should be noted that this is consistent with the fact that the conjugation of the phenyl rings and the cyclopropenium ring diminishes with increase in the twist angle.

The intramolecular distances between the ortho-hydrogens are shown in Figure 2. It is clear that for a

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(17) J. Guy, *J. chim. phys.*, **46**, 469 (1949).

(18) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3345 (1952).

(19) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).

(20) M. J. S. Dewar and H. N. Schmeising, *ibid.*, **11**, 96 (1960).

(21) J. Karle, K. Britts, and S. Brenner, *Acta Cryst.*, **17**, 1506 (1964).

(22) D. A. Bochvar, I. V. Stankevich, and A. L. Chistiakov, *Russ. J. Phys. Chem.*, **33**, 593 (1959).

(23) R. Breslow and H. W. Change, *J. Am. Chem. Soc.*, **83**, 2369 (1961).

**Table VII.** Deviations of the Atoms from the Least-Squares Planes[a]

| | Planes | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| C-6 | *0.000* | *−0.003* | *−0.022* | 0.007 | −0.199 | 0.163 |
| C-7 | *0.000* | *−0.012* | *−0.039* | 0.109 | 0.028 | −0.125 |
| C-8 | *0.000* | *−0.010* | *−0.029* | −0.073 | 0.298 | 0.002 |
| C-9 | 0.001 | *0.007* | *−0.006* | *−0.000* | | |
| C-10 | 0.029 | *0.010* | *−0.026* | | *0.014* | |
| C-11 | 0.021 | *0.010* | *−0.007* | | | *0.000* |
| C-12 | 0.166 | | | *−0.001* | | |
| C-13 | −0.151 | | | *0.000* | | |
| C-14 | 0.457 | | | | *−0.013* | |
| C-15 | −0.393 | | | | *−0.000* | |
| C-16 | 0.278 | | | | | *−0.003* |
| C-17 | −0.218 | | | | | *0.003* |
| C-18 | 0.177 | | | *0.002* | | |
| C-19 | −0.139 | | | *0.001* | | |
| C-20 | 0.515 | | | | *−0.001* | |
| C-21 | −0.347 | | | | *−0.014* | |
| C-22 | 0.306 | | | | | *0.001* |
| C-23 | −0.201 | | | | | *−0.005* |
| C-24 | 0.017 | 0.040 | *0.038* | *−0.002* | | |
| C-25 | 0.136 | 0.103 | *0.050* | | *0.015* | |
| C-26 | 0.067 | 0.051 | *0.042* | | | *0.003* |
| Coefficients[b] | | | | | | |
| *A* | 0.5026 | 0.5084 | 0.5132 | 0.4493 | 0.2861 | 0.6725 |
| *B* | −0.8637 | −0.8603 | −0.8574 | −0.8896 | −0.8984 | −0.7385 |
| *C* | −0.0372 | −0.0366 | −0.0398 | 0.0819 | −0.3331 | −0.0491 |
| *D* | 6.4328 | 6.4148 | 6.3985 | 6.0215 | 7.3357 | 6.1282 |

[a] Atoms included in the calculation of the planes are italicized. [b] $A$, $B$, $C$, and $D$ are coefficients of the planes which are expressed in the form $AX + BY + CZ + D = 0$, where $X$, $Y$, and $Z$ in Å. are measured along $a$, $b$, and $c$.

planar *sym*-triphenylcyclopropenium cation, assuming the above C–C distances, there would be severe compression of the hydrogen atoms. We estimate from the molecular dimensions (using the average values for the C–C bond lengths and angles and the spectroscopic value of 1.07 Å. for the C(sp$^2$)–H bond length) that a twist of the phenyl groups of 13.6° would be sufficient to relieve this compression. Interestingly, this is equal to the mean value of the observed twist angles. Therefore, the triphenylcyclopropenium cation should be expected to be nonplanar even in the isolated state. The variations observed in the twist angles

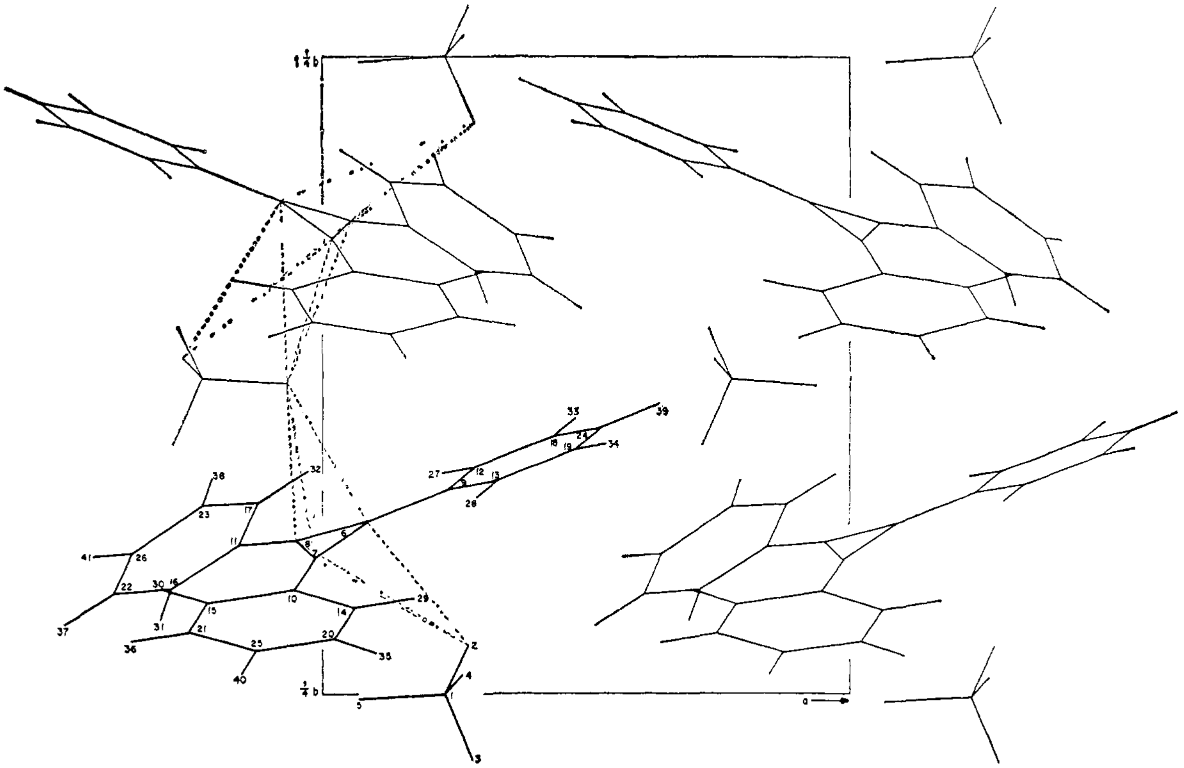

Figure 3. Arrangement of the molecules along one-half of *c* viewed along the *c* axis.

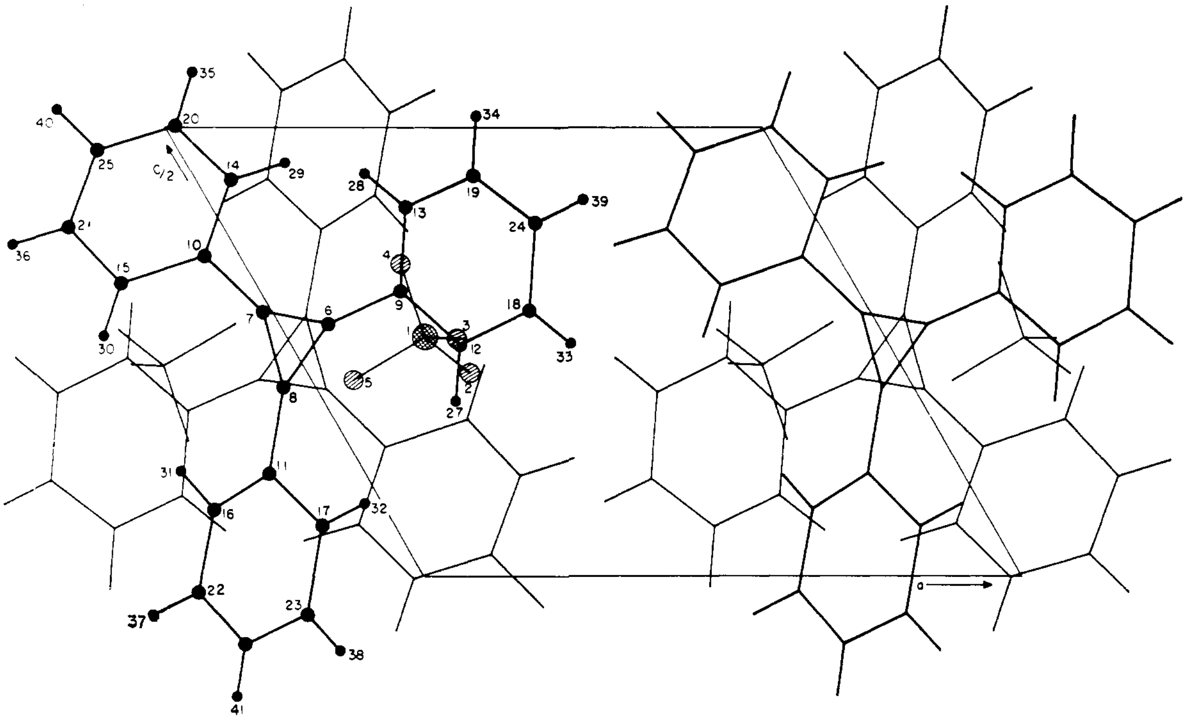

Figure 4. Molecular arrangement as viewed down the *b* axis.

may be attributed to differences in packing about the phenyl groups in the solid.

The atoms attached to the three-membered system are only slightly displaced on the same side of the plane of the cyclopropenium ring. However, the atoms at the *para* positions of C-9, C-10, and C-11 are markedly displaced on the same side of the latter plane. The least-squares plane passing through the atoms C-6, C-7, C-8, C-9, C-10, C-11, C-24, C-25, and C-26 is shown in Table VII, plane 3. It is seen that these atoms do not define a perfect plane. The atoms comprising the phenyl groups lie in a plane (planes 4, 5, and 6, Table VII). Also the atoms of the cyclopropenium ring attached to the phenyl groups lie in the planes of the corresponding phenyl groups, except C-7 which appears to be really displaced. Interestingly, the phenyl ring attached to C-7 displays the largest twist angle as was seen above.

## The Perchlorate

The perchlorate ion executes a large librational motion as seen from the $b_{ij}$ terms of the oxygens (Table II).[24] Hence, it would be expected that the Cl–O bond lengths are markedly affected by the thermal vibration. The approximation made in describing the thermal anisotropy in the oxygens by an ellipsoidal motion is evidently inadequate.

In the Fourier map, "banana"-shaped electron densities were obtained for the oxygens O-2, O-4, and O-5. These electron densities lie approximately in the circumference of the circle passing through the three oxygens. The electron density of O-3 was nearly spherical. Therefore, the perchlorate ion can be visualized as describing a torsional motion about the Cl–O-3 bond.

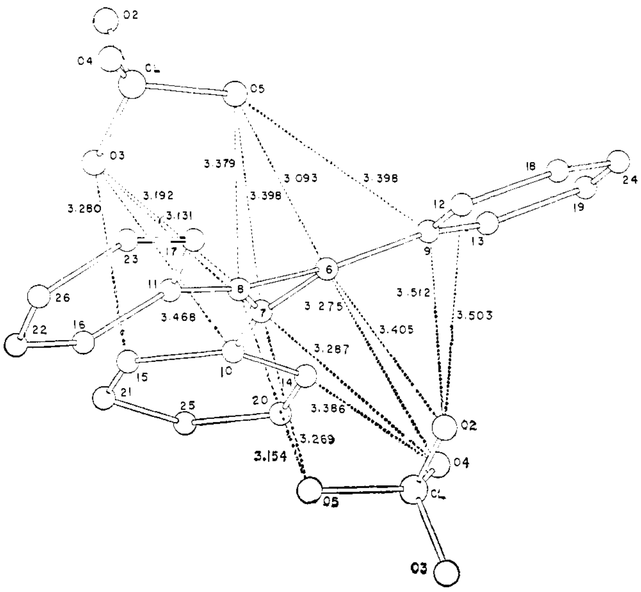

Figure 5. The shortest oxygen–carbon distances.

In the light of the above vibration of the perchlorate, further improvement on the structure was attempted by introducing five split atoms, each one-fifth of the transform of an oxygen atom, to represent the oxygens O-2, O-4, and O-5. The split atoms (approximately 0.3 Å. apart) were placed in arcs, lying in the circle formed by the above oxygens, and about 1.46 Å. from the chlorine atom. The central split atoms were so chosen that their coordinates gave nearly tetrahedral values for the O–Cl–O angles. Based on Gerdil's[25] work, we found that given a temperature factor of 8 Å.$^2$ for the five constituent atoms, placed at distances of 0, ±0.3 and ±0.6 Å., gave a sum total peak that re-

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(24) A list of the magnitudes and direction cosines of the principal axes of the thermal vibration ellipsoids has been deposited with the American Documentary Institute (Document No. 8573).

(25) R. Gerdil, *Acta Cryst.*, 14, 333 (1961).

sembled roughly the oxygen electron densities along the elongated direction. It may be noted that this is only an approximation. Least-squares refinement of the constituent atoms lowered the $R$ to 7.1%. However, the shifts were greater than the error, and the parameters tended to oscillate. Hence the refinement based on "split atoms" was abandoned.

### Intermolecular Distances

The crystal structure can be described as being composed of $TPCP^+$ and $ClO_4^-$ in a zigzag arrangement along the $b$ direction (Figure 3). The carbonium ions are sandwiched by the $ClO_4^-$ groups, while the $ClO_4^-$ (nuts) are held tightly by pairs of cations (nutcrackers). The center of the cyclopropenium ring is nearly coincident with the $2_1$ axis. The molecular arrangement along one-half of the $c$ axis is shown in two views, along the $c$ and $b$ axes (Figures 3 and 4, respectively). The shortest interatomic contacts in the structure are between the electronegative oxygens of the perchlorate and the formally positive carbons of the cyclopropenium ring, as illustrated in Figure 5. Some of these distances would be even shorter if the correct length for the Cl–O distance of 1.46 Å. is assumed.[26] These interactions probably explain the growth of the crystal along the $b$ direction. All other contact distances are greater than the sum of the van der Waals radii of the respective atoms.[27]

**Acknowledgments.** We wish to thank Professor Ronald Breslow for kindly supplying us with the specimen; Drs. J. Stewart, J. Kraut, D. High, R. Chastain, and E. Davidson for the computer programs; and the University Research Computer Laboratory for providing large grants of computer time. This work was supported by Grant GM-10828 of the National Institutes of Health of U. S. Public Health Service.

(26) D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

(27) Note Added in Proof. It is of interest to note that West, Sadô, and Tobbey (1965, private communication) recently have found, by a normal coordinate analysis of the vibrational spectrum of trichlorocyclopropenium cation ($C_3Cl_3^+$), a value of 6.3 mdynes/Å. (considerably greater than that of benzene) for the C–C stretching force constant, indicating that the C–C bond length in the cyclopropenium derivative is in fact shorter than in benzene, and in agreement with our observation

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# Charge-Transfer Complexes of Disulfides with Tetracyanoethylene

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**Abstract:** Using the Benesi–Hildebrand procedure, the association constants and extinction coefficients have been measured for a number of disulfide–TCNE complexes. In the series $n$-alkyl disulfides, $t$-butyl disulfide, and thioctic acid, $K_c$ at 25° increases from ~0.1 to 1.2 l./mole and $-\Delta H$ increases from 0.41 to 7.2 kcal./mole in the order given. The charge-transfer transition energies decrease in the same order. It is proposed that these trends reflect the decreasing angle between the doubly occupied 3p orbitals on the adjacent sulfur atoms of the disulfides. Structures are postulated for the alkyl disulfide and cyclic disulfide complexes, which are considered quantitatively with the aid of semiempirical molecular orbital theory. With an empirically derived estimate for the exchange integral between sulfur 3p and carbon 2p orbitals situated in separate planes, the MO model provides very satisfactory agreement with the observed charge-transfer transitions and transitions assigned to the complexed components.

The donor properties of organic sulfur compounds have been the subject of numerous publications.[1,2] Alkyl sulfides and disulfides form charge-transfer complexes with iodine[3–5] which are more stable than those of the corresponding oxygen compounds.[3c,6] Of the two types of sulfur compound, the sulfides are by far the stronger donors. Inductive effects[1,3c] and a smaller overlap integral[3c,4] for the disulfide complex have been considered as explanations for this difference.

Since the interactions in the ground state of weak complexes are small, absorption bands apart from the charge-transfer transition are observed, which may be ascribed to the complexed components. These bands are generally shifted with respect to those of the uncomplexed components. A variety of interpretations have been advanced for the origin of this shift,[7] and the most reasonable ones appear to be the mutual perturbation of the donor and acceptor energy levels[8] and the removal of restrictions on symmetry-forbidden transitions.[9] McGlynn[5] has studied the ethyl disulfide–iodine complex from this point of view and found the complexed disulfide to have a smaller transition energy than the free disulfide. Using a simple molecular orbital (MO) description of the disulfide molecule, he proposes that the red shift is due to a change in the dihedral angle between the nonbonding, perpendicular 3p orbitals of the two sulfur atoms.

The point of departure for this study was McGlynn's suggestion[5] that the shift of the –S–S– absorption should

(1) R. J. Niedzielski, R. S. Drago, and R. L. Middaugh, *J. Am. Chem. Soc.*, **86**, 1694 (1964); this paper cites much of the earlier literature.

(2) R. S. Drago, B. Wayland, and R. L. Carlson, *ibid.*, **85**, 3125 (1963).

(3) (a) N. W. Tideswell and J. D. McCullough, *ibid.*, **79**, 1031 (1957); (b) J. D. McCullough and D. Mulvey, *ibid.*, **81**, 1291 (1959); (c) H. Tsubomura and R. P. Lang, *ibid.*, **83**, 2085 (1961); (d) R. P. Lang, *ibid.*, **84**, 4438 (1962).

(4) M. Good, A. Major, J. Nag-Chaudhuri, and S. P. McGlynn, *ibid.*, **83**, 4329 (1961).

(5) S. P. McGlynn, J. Nag-Chaudhuri, and M. Good, *ibid.*, **84**, 9 (1962).

(6) M. Tamres and M. Brandon, *ibid.*, **82**, 2134 (1960).

(7) G. Briegleb, "Elektronen-Donator-Acceptor Komplexe," Springer Verlag, Berlin, 1961, Chapter 5.

(8) S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958).

(9) J. Czekalla, *Z. Elektrochem.*, **63**, 1157 (1959).