Structural Studies of Strained Cyclic Esters. Catechol Sulfate

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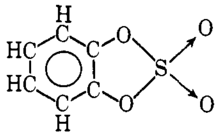
Abstract: The crystal and molecular structure of catechol cyclic sulfate, $C_6H_4SO_4$, has been determined by a single-crystal three-dimensional X-ray diffraction study. This material crystallizes in space group Aba2 with lattice parameters $a = 15.217 \pm 0.010$, $b = 16.167 \pm 0.010$, and $c = 5.562 \pm 0.003$ Å, giving a calculated density $\rho = 1.671$ g cm^{-3} for $Z = 8$. The intensities of 687 unique reflections were measured using the θ–2θ scan mode of a Picker automatic diffractometer (Cu Kα radiation). The structure was solved from the Patterson function and refined by full-matrix least squares to a final discrepancy index $R_1 = 0.090$ for 635 reflections above background. The S, O, and C atoms were assigned anisotropic thermal parameters, and the hydrogen atoms were refined isotropically. Angles in the five-membered ring show the effects of strain: the O–S–O bond angle of 97.1° is substantially below the tetrahedral angle of 109.5°, the O–C–C angles of 110.7 and 112.5° are well below the 120° angle preferred by sp^2 carbon, and the S–O–C bond angles are 108.6 and 108.7°. The exocyclic S–O bond distances are 1.380 and 1.392 Å, the S–O bonds in the ring are 1.585 and 1.601 Å, and the C–O distances are 1.398 and 1.409 Å. The most unexpected feature of the structure is the distortion of the five-membered ring to a nonplanar envelope structure where the sulfur atom lies 0.249 Å above a plane through the six carbon atoms and the two ring oxygen atoms. This result suggests that lone-pair repulsions may play a role in the extraordinarily high rates of alkaline hydrolysis exhibited by five-membered cyclic esters of sulfur and phosphorus as compared to their six-membered or acyclic analogs.

Certain five-membered cyclic esters of sulfur[1-6] and phosphorus[7-11] undergo alkaline hydrolysis at the heteroatom with rates many orders of magnitude faster than their six-membered cyclic or acyclic analogs. Because this effect affords a prime opportunity to establish relationships between molecular structure and reactivity, considerable effort has been expended exploring the structural systematics of these compounds.[4,6,12-15] The discussion of these relationships has focused on two possible causes for the kinetic acceleration: (1) angle strain in the five-membered rings[11] and (2) strain-induced changes in the 2p–3d π character of the endocyclic oxygen–heteroatom bonds.[1,10,16] However, evidence that 1,3 nonbonded interactions between oxygen atoms cause appreciable changes in the total strain energy has been lacking, and the contribution of this effect to the kinetic acceleration has largely been discounted.[1]

Of the cyclic esters of sulfuric acid, the most reliable data on relative rates are for catechol cyclic sulfate[2,5] (I), which has been shown[2] to hydrolyze 2 × 10^7 times faster than its open-chain analog, diphenyl sulfate. The molecular structure of this compound, reported below, shows an unexpected feature. The five-membered ring is puckered into a nonplanar envelope conformation in which the sulfur atom lies above the plane of oxygen and carbon atoms. Because this conformation does not minimize angle strain, this result suggests that the role of 1,3 nonbonded interactions in the kinetic acceleration may deserve reexamination.



I

Experimental Section

A sample of catechol cyclic sulfate, mp 34–35°, was kindly supplied by Kaiser. Crystals grown by sublimation form needles elongated on *c*. These have poorly defined faces and are fairly soft at room temperature. The material blackens upon exposure to X-irradiation with gradual loss of intensity. Because of these experimental difficulties, some care had to be exercised in collecting the data set. We attempted to minimize these problems (1) by performing the X-ray experiment at a reduced laboratory temperature of 18°, (2) by collecting multiple data sets, and (3) by being more selective than usual in accepting weak reflections.

A crystal of approximate dimensions 0.23 × 0.27 × 0.38 mm was sealed in a 0.30-mm diameter thin-wall glass capillary with the *c* axis of the crystal parallel to the capillary axis. The crystal was examined by photographic methods on a Weissenberg goniometer to determine the space group and preliminary lattice constants. The reciprocal lattice symmetry D_{2h} and the reflection conditions $hkl\,(k + l = 2n)$, $0kl\,(k = 2n\ (l = 2n))$, and $h0l\,(h = 2n\ (l = 2n))$ are consistent with space groups Aba2 (C_{2v}^{17}) or Acam (D_{2h}^{18}). The 3.0.0, 5.0.0, and 11.0.0 reflections appeared on the *hk*0 Weissenberg level and were later measured above background on the diffractometer, but closer examination revealed these to be Renninger reflections. More accurate lattice constants, $a = 15.217 \pm 0.010$, $b = 16.167 \pm 0.010$, and $c = 5.562 \pm 0.003$ Å, were obtained by least-squares refinement of setting angles on a four-circle Picker automatic diffractometer. Cu Kα radiation (λ 1.5418 Å) was used. These values give a calculated density $\rho = 1.671$ g cm^{-3} for molecular weight 172.158 and $Z = 8$. No further conclusions about the choice of space group could be drawn at this stage; the

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molecules (of C_{2v} symmetry) could be located in general positions of Aba2 or on either the mirror planes or twofold axes of Acam.

The intensity data were gathered using the θ–2θ scan mode of the diffractometer with Ni-filtered Cu Kα radiation. Two complete data sets (hkl and $\bar{h}kl$) of 687 reflections each were collected out to the instrumental limit $\sin\theta \leq 0.90$. The X-ray tube was placed at a 3° take-off angle, and a detector aperture 4.0 mm square was positioned 30 cm from the crystal. Scan angles of 3° were taken at a scan speed of 2°/min. Background counts of 15 sec were made at each end of the scan by the stationary-crystal–stationary-counter technique. Test reflections were measured after every 50 regular reflections; these declined gradually to 0.90 of the initial value. Decomposition corrections were made based on test reflection intensities. An error

$$\sigma(I) = [(0.03I)^2 + N_0 + k^2N_b]^{1/2} = \sigma(F^2)\mathrm{Lp}$$

was assigned to the net intensity $I = N_0 - kN_b$ of each measurement. Here N_0 is the gross count, N_b is the background count, and k is the ratio of scan time to background time. The intensities were corrected for Lorentz and polarization effects ($F^2 = I/\mathrm{Lp}$) and the redundant data were merged using the algorithms

$$\bar{F} = (F_{hkl}\cdot F_{\bar{h}kl})^{1/2} \text{ if } F_{hkl}, F_{\bar{h}kl} \neq 0$$

$$\bar{F} = F_{hkl}/2 \text{ if } F_{\bar{h}kl} = 0$$

$$\sigma(\bar{F}) = \max\{\sigma(F_{\bar{h}kl}), \sigma(F_{hkl})\}$$

The 50 reflections for which $\sigma(F^2)/F^2 > 0.2$ were arbitrarily defined as absent and were omitted from the least-squares refinement. The linear absorption coefficient of catechol sulfate is 37.83 cm^{-1} for Cu Kα radiation. Transmission coefficients are estimated to vary by less than 10% about a mean value, although an absorption correction was not actually applied. Variations in the $00l$ "ϕ-independent" reflections were in fact less than this amount. Two intense reflections, 4.0.0 and 0.2.0, appeared to show substantial extinction and were dropped from the data set during the course of the refinement.

Solution and Refinement of the Structure

A three-dimensional sharpened Patterson function was computed[17a] based on scale and temperature factors calculated by Wilson's method. A model for the S, O, and C positions, consistent with the acentric space group Aba2, was postulated from this map. This model gave initial values for R_1 and R_2 of 0.384 and 0.569, respectively, where R_1 and R_2 are defined by the relations

$$R_1 = \frac{\sum ||F_o| - F_c||}{\sum |F_o|}$$

$$R_2 = \left\{\frac{\sum w(|F_o| - |F_c|)^2}{\sum wF_o^{\,2}}\right\}^{1/2}$$

$$w = 4F^2/\sigma^2(F^2)$$

Two cycles of full-matrix least-squares refinement[17b,18] of scale and position parameters reduced these values to 0.266 and 0.336, respectively. After five additional cycles in which isotropic temperature factors and positions varied, these figures were further reduced to $R_1 = 0.153$ and $R_2 = 0.207$.

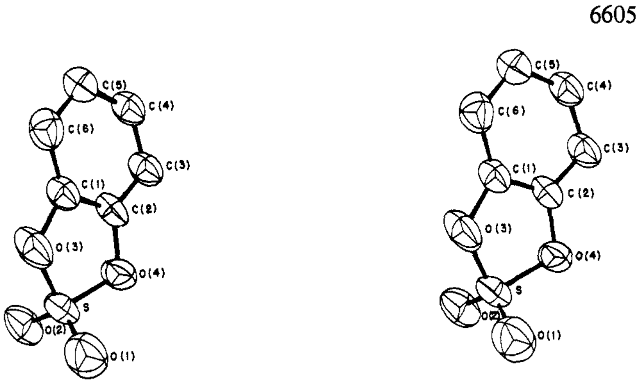

Figure 1. Three-dimensional view of catechol cyclic sulfate showing ellipsoids of thermal motion.

The location of the hydrogen atoms was attempted at this time, but this task proved to be a marginal undertaking. Peak heights in e/Å^3 of H(3), 0.28, H(4), 0.37, H(5), 0.68, and H(6), 0.27, were obtained in a difference Fourier.[17a] Five cycles of additional isotropic refinement on all atoms reduced R_1 to 0.134 and R_2 to 0.172. Then the S, O, and C atoms were given anisotropic thermal parameters while the hydrogens continued to be refined isotropically. Six further cycles of least squares reduced R_1 and R_2 to their final values of 0.090 and 0.107, respectively, for 635 observed reflections. The average parameter shift in the final cycle was 0.05σ, and no nonhydrogen parameter shifted more than 0.15σ. The hydrogen parameters gave large errors during the least-squares refinement and are not considered reliable. The worst results were for H(6) which converged with a temperature factor 24 ± 12 Å^2 at a very short C–H distance. H(5) had a very low temperature factor, although it was reasonably positioned, and H(3) gave too long a bond length. A final difference Fourier revealed no peaks greater than 0.57 e/Å^3. An additional peak of height 0.26 e/Å^3 occurred about 0.5 Å from the expected position of H(6), and about 1.49 Å from C(6).

Final atomic parameters and their standard deviations as computed in the last least-squares cycle are listed in Table I. A table of observed and calculated structure factors is available on request.[19] Bond distances and angles, with standard deviations calculated[17c] from the variance–covariance matrix obtained in the final cycle of least-squares, are shown in Table II. Table III lists the root-mean-square components of thermal displacement along the principal axes, as defined by the anisotropic thermal parameters. The directions of these axes may be inferred from Figure 1, in which the molecular structure is drawn[17d] in three dimensions using 50% probability ellipsoids to represent the thermal motion.

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(19) Material supplementary to this article has been deposited as Document No. NAPS-00501 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 Third Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

Table I. Atomic Parameters[a,b]

Atom	x/a	y/b	z/c	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
S	0.1411 (1)	0.0519 (1)	0.0000 (0)	59 (1)	37 (1)	375 (9)	1 (1)	4 (3)	46 (3)
O(1)	0.2059 (4)	0.1081 (4)	0.0673 (17)	81 (4)	70 (3)	522 (42)	−19 (3)	−5 (11)	34 (11)
O(2)	0.0718 (4)	0.0767 (4)	−0.1428 (17)	69 (3)	61 (3)	505 (35)	8 (3)	−45 (10)	61 (10)
O(3)	0.1852 (4)	−0.2904 (3)	−0.1067 (14)	71 (3)	59 (3)	415 (31)	7 (3)	59 (10)	70 (10)
O(4)	0.1032 (3)	0.0107 (3)	0.2421 (13)	75 (3)	37 (2)	376 (26)	−4 (2)	46 (9)	20 (7)
C(1)	0.1532 (4)	−0.0976 (4)	0.0189 (19)	42 (3)	40 (3)	327 (29)	2 (2)	14 (10)	30 (11)
C(2)	0.1075 (5)	−0.0757 (5)	0.2199 (16)	44 (3)	43 (3)	319 (32)	5 (3)	14 (9)	45 (10)
C(3)	0.0720 (5)	−0.1313 (5)	0.3777 (19)	54 (4)	46 (3)	350 (33)	7 (3)	37 (11)	41 (11)
C(4)	0.0836 (5)	−0.2129 (5)	0.3152 (19)	59 (4)	43 (4)	376 (35)	−3 (3)	16 (12)	40 (10)
C(5)	0.1308 (5)	−0.2379 (5)	0.1110 (19)	55 (4)	41 (4)	388 (35)	3 (3)	−5 (12)	22 (11)
C(6)	0.1675 (5)	−0.1782 (6)	−0.0379 (19)	54 (4)	58 (5)	356 (40)	5 (4)	14 (2)	8 (11)
H(3)	0.0319 (53)	−0.1090 (53)	0.6092 (269)			B^c = 7.4 (2.8) Å^2			
H(4)	0.0650 (37)	−0.2701 (37)	0.4150 (276)			B = 3.2 (1.6)			
H(5)	0.1434 (23)	−0.3016 (24)	0.0894 (94)			B = 0.1 (0.9)			
H(6)	0.1867 (121)	−0.1565 (120)	−0.0484 (955)			B = 23.7 (11.9)			

[a] Standard errors given in parentheses are to be multiplied by 10^{-4}. [b] The anisotropic temperature factors for the S, O, and C atoms are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [c] Isotropic temperature factors for hydrogen.

Table II. Distances and Angles[a]

A. Bond Distances (Å)

Bond	Distance
Bonds to Sulfur	
S–O(1)	1.392 (6)
S–O(2)	1.380 (6)
S–O(3)	1.585 (6)
S–O(4)	1.601 (6)
Carbon–Oxygen Bonds	
O(3)–C(1)	1.398 (9)
O(4)–C(2)	1.404 (9)
Carbon–Carbon Bonds	
C(1)–C(2)	1.363 (13)
C(2)–C(3)	1.368 (11)
C(3)–C(4)	1.375 (12)
C(4)–C(5)	1.404 (13)
C(5)–C(6)	1.389 (12)
C(6)–C(1)	1.359 (13)
Carbon–Hydrogen Bonds	
C(3)–H(3)	1.47 (13)
C(4)–H(4)	1.11 (7)
C(5)–H(5)	1.05 (4)
C(6)–H(6)	0.46 (18)

B. Bond Angles (Degrees)

Vertex	Atom 1	Atom 2	Angle
S	O(1)	O(2)	120.4 (0.4)
	O(1)	O(3)	109.9 (0.4)
	O(1)	O(4)	107.4 (0.5)
	O(2)	O(3)	110.3 (0.5)
	O(2)	O(4)	109.1 (0.4)
	O(3)	O(4)	97.1 (0.3)
O(3)	S	C(1)	108.6 (0.6)
O(4)	S	C(2)	108.7 (0.5)
C(1)	O(3)	C(2)	112.5 (0.6)
	O(3)	C(6)	126.1 (0.9)
	C(2)	C(6)	121.4 (0.7)
C(2)	O(4)	C(3)	125.4 (0.7)
	O(4)	C(1)	110.7 (0.6)
	C(1)	C(3)	123.9 (0.7)
C(3)	C(2)	C(4)	114.7 (0.9)
C(4)	C(3)	C(5)	123.2 (0.7)
C(5)	C(4)	C(6)	119.2 (0.7)
C(6)	C(5)	C(1)	117.6 (0.8)

[a] Standard errors computed from the variance–covariance matrix are given in parentheses.

Table III. Root-Mean-Square Thermal Displacement along Principal Axes[a]

Atom	Axis 1	Axis 2	Axis 3
S	0.180	0.263	0.276
O(1)	0.253	0.290	0.350
O(2)	0.201	0.302	0.333
O(3)	0.185	0.272	0.347
O(4)	0.201	0.239	0.313
C(1)	0.194	0.220	0.260
C(2)	0.181	0.220	0.278
C(3)	0.193	0.231	0.298
C(4)	0.195	0.266	0.279
C(5)	0.216	0.255	0.261
C(6)	0.230	0.251	0.285

[a] Ordered on increasing magnitude.

Description of the Structure

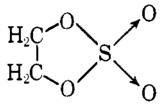
A. Nonplanarity. The most interesting feature of the structure is the nonplanar conformation of the five-membered ring. The sulfur atom lies 0.249 Å above a weighted least-squares plane[17e] through O(3), O(4), and the six carbon atoms (plane 8, Table IV). The maximum deviation from planarity among these eight atoms themselves is only 0.020 Å, which is the

Table IV. Least-Squares Planes[a–c]

	Plane 5	Plane 6	Plane 8	Plane 9
Atom 1	S	C(1)	O(3)	S
Atom 2	O(3)	C(2)	O(4)	O(3)
Atom 3	O(4)	C(3)	C(1)	O(4)
Atom 4	C(1)	C(4)	C(2)	C(1)
Atom 5	C(2)	C(5)	C(3)	C(2)
Atom 6		C(6)	C(4)	C(3)
Atom 7			C(5)	C(4)
Atom 8			C(6)	C(5)
Atom 9				C(6)
m_1	12.974	12.864	12.829	12.921
m_2	1.485	−0.143	−0.148	0.530
m_3	2.860	2.970	2.990	2.931
d	1.959	2.052	2.052	1.950
Δd(atom 1)	−0.051	−0.011	−0.009	−0.099
Δd(atom 2)	0.095	−0.004	−0.006	0.114
Δd(atom 3)	0.088	0.015	−0.016	0.098
Δd(atom 4)	−0.062	−0.010	−0.004	0.032
Δd(atom 5)	−0.047	−0.005	+0.020	0.043
Δd(atom 6)		0.016	−0.006	0.017
Δd(atom 7)			−0.007	−0.059
Δd(atom 8)			−0.007	−0.061
Δd(atom 9)				0.008

[a] Reference 17e. [b] Atom weighted as follows C, 6; O, 8; S, 16. [c] The least-squares planes are defined by the equation $m_1x + m_2y + m_3z = d$.

same order of magnitude as the experimental uncertainty. (A plane through the six atoms of the phenyl group shows a similar maximum deviation of 0.016 Å.) The ring conformation thus approximates an envelope; the dihedral angle between the eight-atom plane above and a plane defined by O(3), S, and O(4) is 13°43′. As a result of this distortion the S–O(1) and S–O(2) bonds form angles of 47° 21′ and 73° 2′, respectively, with plane 8. Nonplanarity has of course been observed in saturated five-membered cyclic esters, since it relieves strain from bond eclipsing. For example, in ethylene sulfate[6] (II) there is a distortion of C_2 symmetry (half-chair) which brings the C atoms above and below a plane through the sulfur and oxygen atoms. Similar distortions are observed in methyl ethylene phosphate[12] (III) and methyl pinacol phosphate[13] (IV). However, in the two structural investigations of unsaturated cyclic esters so far reported, *i.e.*, vinylene sulfate[6] (V) and acetoinediol cyclophosphate[14] (VI), the five-membered rings have been planar. Thus, the C_s type of distortion found in the present structure appears to be unprecedented.



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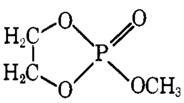

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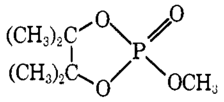

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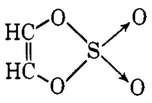

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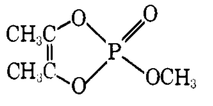
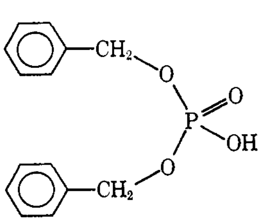


VI

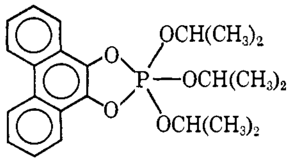
B. Bond Angles. All angles in the five-membered ring show evidence of strain. The O(3)–S–O(4) bond angle of 97.1 ± 0.3° is substantially below the tetrahedral angle of 109.5° and compares fairly closely with other literature values for five-membered cyclic diesters (*cf.* II, 98.4°; III, 99.1°; IV, 98.4°; V, 93.6°; VI, 98.5°). On the other hand, the angle between the two exocyclic oxygens, 120.4°, is substantially greater than the tetrahedral value. The two S–O–C angles, 108.6 ± 0.6 and 108.7 ± 0.5°, have values well below the expected angles for acyclic diesters, such as dibenzylphosphoric acid[20] (VII), where the average P–O–C angle is 120.6°. Similarly, the O–C–C angles in the five-membered ring are strained to values, 112.5 and 110.7° (±0.6°), that are well below the normal 120° angle for sp^2-hybridized carbon.



VII

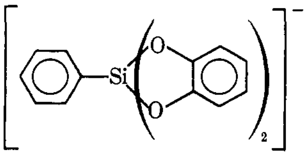
We note that despite the strain evident in these bond angles, the sum of the five internal ring angles is only 537.7°, whereas in a planar conformation this sum must be 540°.

C. π Bonding. Considerable attention has been given to the hypothesis that 2p–3d π bonding between the ring oxygens and the heteroatom plays an essential role in the kinetic acceleration.[1,10,16] Cruickshank has proposed[21] a linear relationship between bond length and multiple-bond character in O–X bonds (X = Si, P, S, Cl) in tetrahedral XO_4^{n-} ions. In catechol cyclic sulfate, the endocyclic O–S bonds have lengths of 1.585 and 1.601 (±0.006) Å. These bond lengths are considerably longer than the value of 1.533 Å reported for the saturated ester ethylene sulfate[6] (II) and are close to the value, 1.616 Å, found in vinylene sulfate[6] (V). Analogous increases in bond lengths of unsaturated *vs.* saturated P–OC bonds have been reported in acetoinediol cyclophosphate[14] (VI) and in a pentaoxyphosphorane[15] (VIII). A possible explanation[15b] for the weakening of these P–O and S–O bonds may be sought in the ability of the aromatic C–C or perhaps even C–O π bonds to compete for the bonding power of the oxygen 2p π electrons.

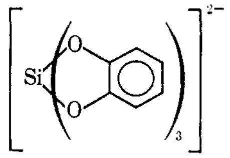


VIII

The C–O bond lengths in catechol cyclic sulfate, 1.398 and 1.404 (±0.009) Å, are slightly shorter than the values reported for the saturated diesters[6,12,13] II–IV, even when the C bond radius is corrected[22] (0.020 Å) for change in hybridization from sp^3 to sp^2. In fact, C–O bonds in unsaturated esters show an interesting range of distances that may indicate an ability to take on considerable multiple-bond character. Examples include V, 1.341; VI, 1.375 (ave.); VIII, 1.347 and 1.433; IX, 1.345 (av); and X, 1.357 (av) Å, where IX[23] and X[24] are catechol derivatives with Si as the heteroatom. The C–C bond lengths in the phenyl ring (Table II) deviate somewhat from the normal[25] aromatic value of 1.395 Å. The differences are of the order of 2–3 standard deviations and may be significant, particularly in view of similar variations in the ions IX and X.



IX



X

D. Molecular Packing. A three-dimensional view[17d] of the molecular packing in catechol cyclic sulfate is given in Figure 2. The crystal structure is dominated by dipolar interactions, with the dipoles aligning head to tail in directions parallel to the centering translations [(*b*/2) ± (*c*/2)]. A list of intermolecular contact dis-

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[20] J. D. Dunitz and J. S. Rollett, *Acta Cryst.*, **9**, 327 (1956).

[21] D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

[22] L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963, p 39.

[23] F. P. Boer, J. J. Flynn, and J. W. Turley, *J. Am. Chem. Soc.*, **90**, 6973 (1968).

[24] F. P. Boer and J. J. Flynn, submitted for publication.

[25] "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

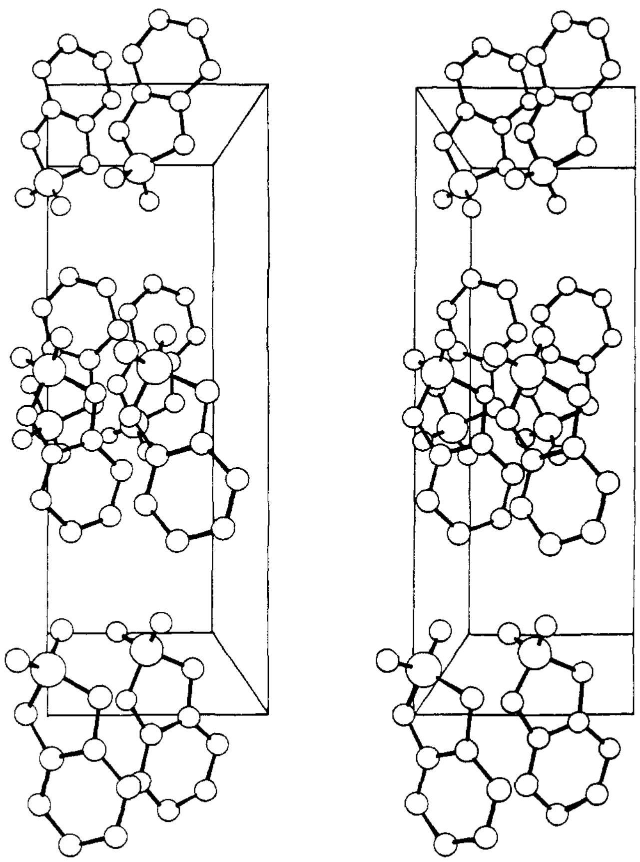


Figure 2. Three-dimensional view of molecular packing in catechol cyclic sulfate as viewed down the x axis. y is vertical and z horizontal.

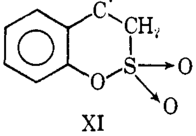
tances is given in Table V. None of these is exceptionally short. There are a variety of O···O and O···C contacts, but the crystal seems to avoid close contact between the phenyl groups: the shortest C···C contact is 3.737 Å.

Table V. Selected Intermolecular Contacts

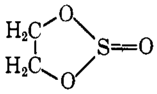
Atom 1	Atom 2	Distance	Transform, atom 2
S	O(1)	3.470	$\frac{1}{2} - x, y, -\frac{1}{2} + z$
S	O(3)	3.672	$\frac{1}{2} - x, y, \frac{1}{2} + z$
O(1)	O(1)	3.088	$\frac{1}{2} - x, y, -\frac{1}{2} + z$
O(1)	O(3)	3.309	$\frac{1}{2} - x, y, \frac{1}{2} + z$
O(1)	C(5)	3.526	$\frac{1}{2} - x, \frac{1}{2} + y, z$
O(2)	O(2)	3.304	$-x, -y, z$
O(2)	C(2)	3.394	$-x, -y, z$
O(2)	C(4)	3.415	$x, \frac{1}{2} + y, -\frac{1}{2} + z$
O(2)	C(5)	3.415	$x, \frac{1}{2} + y, -\frac{1}{2} + z$
O(2)	C(1)	3.556	$-x, -y, z$
O(2)	C(3)	3.561	$-x, -y, -1 + z$
O(3)	C(2)	3.384	$\frac{1}{2} - x, y, -\frac{1}{2} + z$
O(3)	O(4)	3.390	$\frac{1}{2} - x, y, -\frac{1}{2} + z$
O(3)	C(1)	3.408	$\frac{1}{2} - x, y, -\frac{1}{2} + z$
O(3)	O(3)	3.410	$\frac{1}{2} - x, y, -\frac{1}{2} + z$
O(4)	O(4)	3.158	$-x, -y, z$
O(4)	C(2)	3.376	$-x, -y, z$
O(4)	C(3)	3.388	$-x, -y, z$

E. Relation to Kinetic Acceleration. The nonplanar structure observed for catechol cyclic sulfate may arise from either of two effects. The first, crystal-packing forces, cannot be entirely discounted. This explanation seems the less likely in view of the absence of short intermolecular contacts, the relatively large amplitudes of thermal motion, and the lack of any other evidence for molecular distortions induced by crystal forces.

1,3-Nonbonded interactions are the alternative cause. If the lone pairs of the oxygen atoms should be tetrahedrally disposed,[26] their lobes will, in a planar ring, eclipse the exocyclic S–O bonds. These short bonds have considerable multiple-bond character and thus high electron density. Such an effect can be of general importance in the kinetic acceleration, for six-membered cyclic and acyclic esters are free to minimize these interactions by staggering lobes of high-electron density. In fact, the structures of the acyclic diester[20] VII and the six-membered cyclic sultone[4] XI suggest these 1,3-nonbonded interactions are indeed minimized when the molecule has the opportunity to do so.



XI



XII

In the five-membered cyclic esters 1,3-nonbonded interactions can be reduced by bending into a nonplanar envelope conformation, but only at the expense of additional Baeyer strain. Whether this occurs appears to depend on a fine balance of forces, for the unsaturated esters V and VI are observed to be planar.[6,14] We of course do not mean to suggest that lone-pair–bond-pair repulsions account for the whole effect; all the evidence suggests that angle strain is present and is very considerable. In this regard, it is worth noting that Usher, Dennis, and Westheimer have reproduced[11] the experimental conformation of methyl ethylene phosphate (III) with some success taking into account only angle bending and bond-pair–bond-pair repulsive forces. We note also that Davis[27] has shown that no thermochemical strain, or kinetic acceleration, occurs in ethylene sulfite (XII), where the S–O bond approximately bisects the angle between the oxygen lone-pair lobes. His results and calculations led to the conclusion that 1,3 interactions were negligible in the sulfite system, but pointed out at that time the possibility of 1,3 interactions when *four* oxygen atoms were bound to sulfur or phosphorus.

The situation with respect to 2p–3d π bonding is less clear. Because P^{31} nuclei in strained cyclic esters appear in the nmr to be less shielded than in unstrained compounds,[16] it was thought for a time that ring strain reduces 2p–3d π bonding between phosphorus and oxygen atoms.[1,10,16] However, ring strain created no discernible difference[12,13] in the exocyclic and endocyclic P–OC bond lengths of compounds III and IV, so this effect does not appear to be corroborated by the experimental data. A similar problem is associated with the comparison of alkoxy- and aryloxy-substituted phosphates: the P^{31} chemical shifts are more positive for the aryloxy compounds.[16] These data have been interpreted to suggest that dπ–pπ overlap is enhanced by conjugation with the aromatic system. The available metric data do not corroborate this assumption: we have seen that S–O and P–O bond lengths are signif-

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(26) J. W. Linnett, "The Electronic Structure of Molecules," John Wiley and Sons, Inc., New York, N. Y., 1964, pp 30, 31.

(27) R. E. Davis, *J. Am. Chem. Soc.*, **84**, 599 (1962).

icantly *longer* for unsaturated esters. The available data do suggest that there are significant changes in multiple-bond character in the various cyclic esters, but these changes appear to be electronic in origin and do not seem to be induced by ring strain.

Acknowledgment. We are grateful to Professor E. T. Kaiser for supplying the compound and some helpful commentary, and are also pleased to acknowledge valuable discussions with Drs. Francis Johnson and Steven W. Tobey.

The Reaction of $(CF_3P)_4$ with Some Compounds with Nonmetal–Nonmetal Bonds

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Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. Received January 2, 1969

Abstract: The cyclotetraphosphine $(CF_3P)_4$ reacts with $(CH_3)_4As_2$ and $(CH_3)_2S_2$ to insert a CF_3P group into the As–As or S–S bond. A variety of products was formed by the action of $(CF_3P)_4$ on $(CH_3)_2NP(CH_3)_2$ with the major component being the phosphinidene complex $(CH_3)_2N(CH_3)_2P\rightarrow PCF_3$. Tetramethylhydrazine behaves like $(CH_3)_3N$ in that it catalyzes the interconversion of $(CF_3P)_4$ and $(CF_3P)_5$. However, no N–N bond cleavage was detected. No reaction takes place between $(CF_3P)_4$ and $(CH_3)_6Si_2$ up to 138°. The temperature dependence of the pmr spectrum of the diarsinophosphine, $[(CH_3)_2As]_2PCF_3$, has been studied. The spectral changes are ascribed to a bimolecular exchange reaction.

The present work was undertaken as part of a general program of investigation of the carbenoid behavior of phosphinidene (RP) groups. This particular paper is concerned with attempts to insert the CF_3P moiety into various nonmetal–nonmetal bonds.[2] Prior to our work, Schmidt and Osterroht[3] reported the insertion of a C_6H_5P group into a sulfur–sulfur bond.

Experimental Section

All volatile materials were handled in high-vacuum manifolds with U-traps interconnected by mercury float valves or Apiezon-greased stopcocks. Materials of low volatility were handled under a dry nitrogen atmosphere or in a helium-filled drybox.

Materials. The compounds $(CF_3P)_4$,[4] $(CH_3)_4As_2$,[5] B_2H_6,[6] $(CH_3)_2NP(CH_3)_2$,[7] $[(CH_3)_2P]_2PCF_3$,[2] and $[(CH_3)_2N]_2PCF_3$[8] were made and purified according to literature methods. Tetramethylhydrazine was kindly donated by Dr. W. E. Thun of the Naval Weapons Center, China Lake, Calif. Hydrogen chloride, $(CH_3)_6Si_2$, and $(CH_3)_2S_2$ were procured commercially and used without subsequent purification. The solvents C_6H_6 and C_6D_{12} were distilled prior to use.

The Reaction of $(CF_3P)_4$ with $(CH_3)_4As_2$. A mixture of 0.536 g (2.553 mmoles) of $(CH_3)_4As_2$ and 2.696 g (0.624 mmole) of $(CF_3P)_4$ was sealed in an evacuated ampoule at −196° and allowed to warm slowly to ambient temperature. The initial yellow color of the solution faded after a few minutes. After standing overnight at ambient temperature the ampoule was opened and the traces of volatiles were pumped off to leave an essentially quantitative yield of clear, colorless bis(dimethylarsino)trifluoromethylphosphine (I). *Anal.* Calcd for $C_5H_{12}As_2F_3P$: C, 19.37; H, 3.90. Found: C, 19.26; H, 4.06. The vapor tension of I is 0.5 mm at 24°. The ^1H and ^{19}F nmr data for I are presented in Table I. The ir spectrum of I (liquid film) consisted of peaks (cm^{-1}) at 2979, 2910, and 2805 in the C–H stretching region, 1420 and 1258 in the CH_3 deformation region, and 1167, 1122, and 1093 in the C–F stretching region. The CH_3 rock and wag occurred at 895 and 842, the CF_3 symmetrical deformation at 732, the As–C stretch at 576, the CF_3 asymmetric deformation at 563, and the P–C stretch at 435. The vapor-phase uv spectrum of I displays maxima at 2194 and 2484 Å.

The Reaction of $[(CH_3)_2As]_2PCF_3$ (I) with HCl. The reaction $2HCl + [(CH_3)_2As]_2PCF_3 \rightarrow CF_3PH_2 + 2(CH_3)_2AsCl$ occurred essentially quantitatively, thus further confirming the formula of I. In this experiment 0.1585 g (0.511 mmole) of I consumed 1.023 mmoles (from 1.050) of HCl upon slow warming from −196° to form 0.937 mmole of $(CH_3)_2AsCl$ (91.6% yield) and 0.506 mmole of CF_3PH_2 (99.0% yield). The $(CH_3)_2AsCl$ was identified by comparison of its ir and pmr spectra with those of a known sample of this compound. Identification of CF_3PH_2 was made on the basis of its vapor tension[4] of 45 mm at −78.5° and a pmr spectrum. The latter (neat liquid) consists of a pair of quartets centered at τ 6.48 with $J_{PH} = 199.99$ Hz and $J_{FCPH} = 11.90$ Hz.

The Reaction of $[(CH_3)_2As]_2PCF_3$ (I) with B_2H_6. A mixture of 0.1633 g (0.527 mmole) of I and 0.863 mmol of B_2H_6 was allowed to warm slowly from −196° in a sealed ampoule. Removal of the excess B_2H_6 (0.270 mmole) left the viscous colorless liquid bisborane adduct $[(CH_3)_2As]_2PCF_3\cdot 2BH_3$ (II). *Anal.* Calcd for II: C, 17.79; H, 5.37. Found: C, 17.92; H, 5.57. The ^{11}B nmr spectrum of II (TMS solution) displayed a broad singlet at +20.6 ppm relative to external $B(OCH_3)_3$.

The Reaction of $(CF_3P)_4$ with $(CH_3)_2S_2$. A mixture of 0.1790 g (0.448 mmole) of $(CF_3P)_4$ and 0.3285 g (3.487 mmoles) of $(CH_3)_2S_2$ was allowed to warm slowly from −196° in an evacuated, sealed nmr tube containing a capillary of CCl_3F. After standing approximately 12 hr at ambient temperature the ^{19}F nmr spectrum was recorded. This indicated that approximately 20% conversion of $(CF_3P)_4$ to $(CF_3P)_5$ had occurred and that a small amount of $(CH_3S)_2PCF_3$ (III) had been formed. The CF_3P insertion reaction was completed by heating the tube at 143° for 1 hr. Fractionation of the volatiles with U-traps held at −25 and −196° resulted in the condensation of 0.1667 g (0.859 mmole) of III in the −25° trap. A further 0.1462 g (0.753 mmole) of III was isolated by using a −35° trap. The total amount of III (1.612 mmoles) represented a 90.1% yield. Identification of III was made on the basis of the conformity of its vapor tension and ir spectral data with the literature values.[9] The nmr data for III are presented in Table I.

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(1) National Science Foundation Undergraduate Participant, Summer, 1968; Welch Undergraduate Research Participant, Long Session, 1967–1968.

(2) For a preliminary report of this work, see A. H. Cowley, *J. Am. Chem. Soc.*, **89**, 5990 (1967).

(3) U. Schmidt and C. Osterroht, *Angew. Chem. Intern. Ed. Engl.*, **4**, 437 (1965); U. Schmidt, *et al.*, *Chem. Ber.*, **101**, 1381 (1968). For a review of related work on phosphinidene chemistry, see O. M. Nefedov and M. N. Manakow, *Angew. Chem. Intern. Ed. Engl.*, **5**, 1021 (1966).

(4) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958).

(5) V. Auger, *Compt. Rend.*, **142**, 1153 (1906).

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(8) J. F. Nixon and R. G. Cavell, *J. Chem. Soc.*, 5983 (1964).

(9) A. B. Burg and K. Gosling, *J. Am. Chem. Soc.*, **87**, 2113 (1965).