

water (15 ml.) was added, and the hydrazone was extracted with chloroform. This chloroform extract was evaporated to dryness and the residue was dissolved in diethylene glycol (3 ml.). After addition of sodium hydroxide (ca. 50 mg.) the solution was heated in an oil bath (220°) for 3.5 hr. Water was added and the basic material was extracted with chloroform. After evaporation and sublimation (100° at 0.01 mm.) of the crude extract white crystals (VII, ca. 0.5 mg.) were obtained: R_f 0.20; mass spectrum m/e 306 (M^+), 291, 265, 238, 223, 209, 194, 182, 169, 153, 152.5, 144, 138, 109, and 96.

Pyrolysis of N_α -Methylkopsinyl Tosylate (X) to N_α -Methylkopsinylene (XII) and N_α -Methylkopsane (VII). N_α -Methylkopsinyl alcohol (10 mg.) was dissolved in pyridine (5 ml.) and *p*-toluenesulfonic anhydride (80 mg.) was added. After standing at room temperature for 18 hr., water was added, and the reaction mixture was evaporated (at 90°) and extracted several times with chloroform. The combined extracts were washed and purified by chromatography on silicic acid (1 g., 100 mesh) using chloroform as eluent, R_f 0.56. Kept at 100° (1 hr., 2×10^{-6} mm.) the tosylate decomposed giving N_α -methylkopsinylene¹³ (XII, ca. 10–20% yield, R_f 0.32) and N_α -methylkopsane (VII, ca. 10–20% yield, R_f 0.20) in addition to starting material (ca. 50–70%). N_α -Methylkopsinyl tosylate decomposed in the mass spectrometer (at 90°) giving a spectrum being almost identical with that of N_α -methylkopsane (some contamination with N_α -methylkopsinylene).

Pyrolysis of N_α -Methylkopsinyl Iodide (IX) to N_α -Methylkopsinylene (XII) and N_α -Methylkopsane (VII). N_α -Methylkopsinyl alcohol (XI, 50 mg.) was dissolved in freshly distilled hydriodic acid (5 ml.) and red phosphorus (250 mg.) was added. This mixture was

(13) Mass spectrum and R_f value identical with an authentic sample kindly supplied by Professor G. Büchi.

kept under nitrogen in an oil bath at 140° for 30 hr. The solution was neutralized with sodium carbonate and adjusted to pH 10. After extraction with chloroform and evaporation, the reaction product was separated from starting material by chromatography on silicic acid (2 g., 100 mesh) using methanol–chloroform (1:99) as eluent to give N_α -methylkopsinyl iodide (IX, 20 mg., R_f 0.51), mass spectrum m/e 434 (M^+). The iodide was pyrolyzed at 90° (1.5 hr., 0.01 mm.). The reaction product was separated by thin layer chromatography yielding undecomposed starting material (70–80% yield, R_f 0.51), N_α -methylkopsinylene (XII, 10–15% yield, R_f 0.32), and N_α -methylkopsane (VII, 10–15% yield), R_f 0.20; mass spectrum 306 (M^+), 291, 238, 223, 209, 194, 182, 169, 153, 152.5, 144, 138, 109, and 96; infrared 2940 (s), 1605 (m), and 1490 (m) cm^{-1} ; ultraviolet λ_{max} 255 and 303 $m\mu$; λ_{min} 231 and 277 $m\mu$.

Cleavage of Alkaloid B (IB) by Alkali to Pleiocarpinilam (XIII). Alkaloid B (10 mg.) was refluxed for 2 hr. with 4 ml. of methanolic sodium hydroxide. After evaporation to dryness the residue was suspended in water and extracted with chloroform. The aqueous layer was evaporated to dryness, methanol (10 ml.) was added, and gaseous hydrochloric acid was bubbled through this solution for 2.5 hr. while it was heated to reflux. The methanol was removed by evaporation, water (10 ml.) was added, and the pH was adjusted to 10 with sodium carbonate. The basic material was extracted with chloroform and purified by thin layer chromatography. It was found to be identical with pleiocarpinilam (XIII)¹¹ on the basis of infrared and mass spectra and mobility on t.l.c.

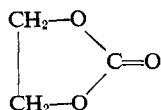
Acknowledgment. We are indebted to Dr. Frank A. Hochstein (Charles Pfizer) for the crude bark extract. This work was supported by a research grant from the National Science Foundation (GP 3734).

Communications to the Editor

The Planarity of the Ring Atoms in Ethylene Carbonate

Sir:

An X-ray diffraction study¹ of ethylene carbonate



has shown the molecule in the solid state to have C_2 symmetry, with the CO_3 moiety forming a plane and the C–C bond in the ethylenic part of the molecule at an angle of about 20° to the CO_3 plane. Angell² has made a very interesting suggestion, based on the infrared spectrum of the molecule, that the symmetry changes to C_{2v} when the solid is melted, dissolved, or vaporized, and that the entire molecule with the exception of the

hydrogen atoms becomes coplanar. His evidence comes from the disappearance of bands at 1008, 1225, and 3030 cm^{-1} in the gas, liquid, and solution spectra, these bands being allowed for C_2 symmetry but infrared inactive for C_{2v} . Simon and Heintz³ have also investigated the infrared and Raman spectra of ethylene carbonate and come to the same conclusion. The reported change of symmetry between the solid and other phases is quite unusual and seemed to warrant further study.

Microwave spectroscopic techniques provide a very sensitive test for strict planarity. If the molecule is not planar, the potential function for the ring-puckering vibration has a double minimum. Provided the barrier at the planar configuration is sufficiently low, tunneling through the barrier causes the energy levels to be split with a consequent doubling of the observed

(1) C. J. Brown, *Acta Cryst.*, **7**, 92 (1954).

(2) C. L. Angell, *Trans. Faraday Soc.*, **52**, 1178 (1956).

(3) A. Simon and G. Heintz, *Chem. Ber.*, **95**, 2333 (1962).

lines in the spectrum. A second test for planarity comes from the measured moments of inertia, since the out-of-plane contributions to the moments are measured by $\Sigma m_i c_i^2 = \frac{1}{2}(I_a + I_b - I_c)$, where m_i is the mass of the i th atom, c_i is its out-of-plane distance, and the I values are the three moments of inertia.

Table I. Observed and Calculated Transition Frequencies

Transition	ν_{obsd} , Mc.	ν_{calcd} , Mc.	$\nu_{\text{calcd}} - \nu_{\text{obsd}}$, Mc.
1 ₁₁ → 2 ₁₂	12,003.38	12,033.29	-0.09
	...	12,009.09	...
1 ₀₁ → 2 ₀₂	12,933.70	12,933.48	-0.22
	12,938.12	12,938.43	+0.31
	14,261.14	14,260.99	-0.15
1 ₁₀ → 2 ₁₁	14,264.27	14,264.23	-0.04
	17,889.99	17,890.04	+0.05
2 ₁₂ → 3 ₁₃	17,898.63	17,898.98	+0.35
	18,941.14	18,941.18	+0.04
2 ₀₂ → 3 ₀₃	18,949.25	18,949.53	+0.28
	19,698.00	19,698.21	+0.21
2 ₂₁ → 3 ₂₂	19,704.74	19,704.99	+0.25
	20,455.35	20,455.24	-0.11
2 ₂₀ → 3 ₂₁	20,460.58	20,460.45	-0.13
	21,254.34	21,254.33	-0.01
2 ₁₁ → 3 ₁₂	21,259.80	21,259.50	-0.30
	23,666.77	23,667.28	+0.51
3 ₁₃ → 4 ₁₄	23,680.03	23,679.56	-0.47
	24,563.32	24,563.72	+0.40
3 ₀₃ → 4 ₀₄	24,576.08	24,575.99	-0.09
	26,107.30	26,108.58	+1.28
3 ₂₂ → 4 ₂₃	...	26,117.96	...

The observed microwave spectrum of ethylene carbonate was quite rich, with many observable transitions from molecules in excited vibrational states. Particularly prominent in the spectrum were closely spaced doublets of considerably greater intensity than the other lines. The frequencies of these were measured, and they were found to fit rigid rotor patterns for low- J ,

Table II. Calculated Rotational Constants and Moments of Inertia^a

	Lower frequency set	Higher frequency set
A , Mc.	8044.3	8045.1
B , Mc.	3847.46	3847.95
C , Mc.	2718.61	2720.38
I_a , a.m.u. Å. ²	62.824	62.818
I_b , a.m.u. Å. ²	131.353	131.337
I_c , a.m.u. Å. ²	185.895	185.774
$\frac{1}{2}(I_a + I_b - I_c)$, a.m.u. Å. ²	4.141	4.191

^a Conversion factor: $I_a = 5.05377 \times 10^8/A$, corresponding to $C^{12} = 12$ atomic weight scale.

R-branch transitions. From their intensity, they must be considered to arise from the two lowest vibrational states split by tunneling. The measured frequencies are listed in Table I together with the frequencies cal-

culated from the derived rotational constants given in Table II.

The data provide two independent kinds of evidence that ethylene carbonate has a nonplanar ring in the gas phase and that the reported symmetry difference between the gas and solid phases is not present. First, the appearance of doublets of similar intensity for the rotational transitions can be explained only by the assumption of a nonplanar ground state with tunneling through the barrier at the planar configuration. Secondly, the observed out-of-plane contribution to the moments of inertia is too large to arise from the hydrogen atoms only. If a C-H bond length of 1.096 Å. and tetrahedral angles are assumed, $\frac{1}{2}(I_a + I_b - I_c)$ can be calculated to be 3.229 a.m.u. Å.². Propiolactone, which does have a planar ring with the same number of out-of-plane hydrogen atoms, has been shown⁴ to have $\frac{1}{2}(I_a + I_b - I_c) = 3.242$ a.m.u. Å.² in the ground state. The values of 4.141 and 4.191 measured for ethylene carbonate must contain an appreciable contribution from the heavier atoms since they would otherwise represent impossibly large hydrogen distances or angles.

As the ring approaches planarity, the intensities of the infrared transitions that are inactive in the C_{2v} limit must become weaker. If the ring is more nearly planar in the liquid and vapor states it may be that the intensity of these bands falls below the observable limit even though they are not forbidden by symmetry.

Acknowledgment. This research was made possible by support extended by the Robert A. Welch Foundation.

(4) D. W. Boone, C. O. Britt, and J. E. Boggs, *J. Chem. Phys.*, **43**, 1190 (1965).

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Received August 30, 1965

Metal Complexes of Tertiary Phosphine Sulfides¹

Sir:

A variety of interesting phosphine oxide² complexes have been investigated during the past 7 years. Since tertiary phosphine sulfides possess unshared pairs of electrons on the sulfur atom and have approximately the same structures as analogous phosphine oxides, one would expect tertiary phosphine sulfides also to form stable transition metal complexes. In fact, Zingaro, *et al.*,^{3,4} demonstrated that phosphine sulfides

(1) Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research through Grant No. 1518-A1,3.

(2) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961); E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 1878 (1960); *ibid.*, 2276 (1960).

(3) R. A. Zingaro and R. M. Hedges, *J. Phys. Chem.*, **65**, 1132 (1961).

(4) R. A. Zingaro, R. E. McGlothlin, and E. A. Meyers, *ibid.*, **66**, 2579 (1962).