TABLE I

MASS SPECTRUM OF IV[a]

m/e	Ion$^+$	% of m/e 91	Remarks
450	$C_{30}H_{26}S_2$ (M)	3.0	$\frac{M + 1}{M}$ = 34.4% (calcd 34.4%) $\frac{M + 2}{M}$ = 16.4% (calcd 14.0%)
386	M − S_2	9.3	
385		18.8	
384		22.0	
383		6.9	
382		18.0	
331*	Metastable		$M^+ \rightarrow (M - S_2)^+$ (calcd 331.1)
296	M − S_2 − C_7H_6	36.4	
294	M − S_2 − C_7H_8	51.4	
205	M − S_2 − (C_7H_6 + C_7H_7)	57.5	
180	$C_6H_5CH{=}CHC_6H_5$	68.6	
128	$C_6H_5C_4H_3$	56.4	
121	C_6H_5CS	57.3	
115	$C_6H_5C_3H_2$	39.1	
91	C_7H_7	100.0 (B)	
78	C_6H_6	24.1	
77	C_6H_5	37.5	
44	CS	232	
34	H_2S	113.6	
33		50.9	
32		55.0	

[a] The strong metastable ion was found on an early spectrum taken on a Consolidated 21-103C mass spectrometer. That spectrum also showed a strong peak at m/e 312 (27.3% of m/e 91) corresponding to 2,3,5-triphenylthiophene, M + 1/M = 27.7%, M + 2/M = 7.9%.

octane (IV), mp 141–143°. Three crystallizations from petroleum ether yielded 19 mg of analytically pure IV: mp 143–145°; $\lambda_{max}^{ethanol}$ 212 nm (ϵ 32,200); ν_{max}^{KBr} 696, 733, 762, 773, 909, 948, 1031, 1083, 1154, 1183, 1209, 1251, 1267, 1297–1308 (broad), 1449, 1454, 1496, 1586, 1602, 2920, 2985, 3033, and 3070 cm^{-1}.

Anal. Calcd for $C_{30}H_{26}S_2$ (450.67): C, 79.96; H, 5.82. Found: C, 79.72; H, 6.19.

1,4,5,7-Tetraphenyl-2,3-dithiabicyclo[2.2.2]octane (IV), mp 140–145°, was also obtained in low yield from an ether solution of *cis*-1,2-diphenylcyclopropanethiol[1d] that had been allowed to stand at room temperature for 59 days. Isolation was accomplished by chromatography on silica gel and purification by crystallization from petroleum ether (see Table I).

1,3-Diphenyl-1-propanone (V).—Successive elution of the column with 30:70, 35:65, and 40:60 benzene–petroleum ether yielded no crystalline materials. Elution with 75:25 benzene–petroleum ether gave 1.0 g of a viscous yellow oil. Thin layer chromatography showed that this material was a mixture of six components. Further elution with 75:25 benzene–petroleum ether yielded 15 mg of 1,3-diphenyl-1-propanone, mp 60–70°. Crystallization from petroleum ether gave pure V, mp 70–71°. A mixture with an authentic sample, mp 71–72°, of V showed no depression in melting point. The 2,4-dinitrophenylhydrazone had mp and mmp 184–187°.

2,3,5-Triphenylthiophene (II).—The method of Smith[3] was duplicated. The crude product, mp 90–100°, was purified by chromatography on silica gel and elution with petroleum ether. The chromatographed product, mp 127–132°, was further purified by repeated crystallizations from petroleum ether. The purified 2,3,5-triphenylthiophene (II), mp 143.5–144°, was identical in all respects (melting point, mixture melting point, and uv and ir spectra) with that isolated from the reaction of *trans*-2,4-diphenylthietane (I) with potassium *tert*-butoxide. Reported melting points are 127[3] and 198°.[4]

Registry No.—I, 24609-88-9; II, 20851-07-4; III, 3383-32-2; IV, 30158-27-1; V, 1083-30-3.

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Concerning Internal Rotation in Diarylalkynes

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In diarylalkynes the question arises concerning the relative orientation of the two aromatic rings. One possibility is that the p orbitals of both aromatic rings overlap the same set of p orbitals of the alkyne. This leads to the planar geometry illustrated in Figure 1. A second possibility is that the π system of one aromatic ring overlaps one set of p orbitals of the alkyne while that of the second aromatic ring overlaps the other. This results in the perpendicular geometry shown in Figure 2. A third possibility is that no single orientation is preferred and that, due to the cylindrical symmetry of the alkyne, a freely rotating system occurs; see Figure 3.

In the freely rotating case, the system must pass through both the coplanar and the perpendicular geometries, and the internal rotation is truly free only if these two have the same energy. Thus the problem reduces to finding the energies of the coplanar and perpendicular forms of the diarylalkyne. If one form has a lower energy, the molecule exists in that geometry. If the two forms have the same energy, a freely rotating

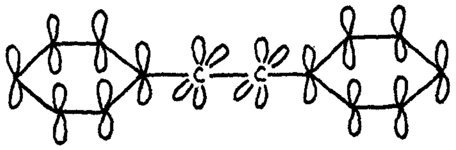


Figure 1.—Coplanar form of diphenylacetylene.

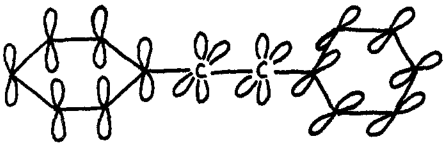
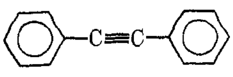


Figure 2.—Perpendicular form of diphenylacetylene.

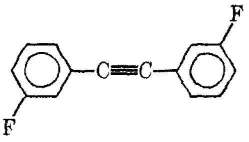
species occurs. Possible reaction coordinates are given in Figure 4, where θ is the dihedral angle.

Quantum mechanical calculations were carried out to investigate these possibilities. Since in all conformations the σ system of the aromatic rings interacts with at least one of the π systems of the alkyne, it was thought unwise to do a simple π-electron calculation. Instead the CNDO and INDO methods of Pople were used.[1-3] These methods look at all the valence electrons.

The CNDO results for rotational problems have been discussed by Pople and Segal who performed calculations on ethane, methanol, and methylamine.[2] Their calculations show that in all three cases the staggered form has a lower energy than the eclipsed, the barriers being 1.79 kcal/mol, 0.67 kcal/mol, and 1.21 kcal/mol, respectively. The experimental values are 3.0 kcal/mol,[4] 1.07 kcal/mol,[5] and 1.98 kcal/mol.[5] It appears that the CNDO approach gives excellent results for rotational problems. Calculations were performed on diphenylacetylene (1) and on bis(3′-fluorophenyl)acetylene (2).



1



2

Robertson and Woodward[6] have made an X-ray crystallographic study on **1**, and their bond distances and bond angles were used in the calculations. Their values are given in Figure 5.

The carbon–hydrogen distance used was 1.09 Å, the value found in benzene, while for **2**, the carbon–fluorine distance was 1.30 Å, the value in fluorobenzene. The nuclear coordinates were obtained for the different geometries by rotating one of the aromatic rings through the required angle. The results are presented in Tables I and II. The energy is in hartrees (h). For **2**, the calculated dipole moments, which are also presented, are in excellent agreement with the values obtained by vectorial addition of group moments.

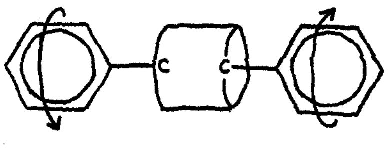
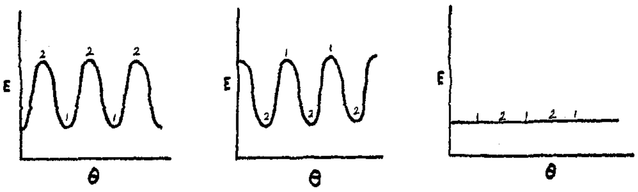


Figure 3.—Freely rotating form of diphenylacetylene.



Coplanar Form more stable

Perpendicular Form more stable

Freely Rotating

Figure 4.—Reaction coordinates for the internal rotation of diarylalkynes.

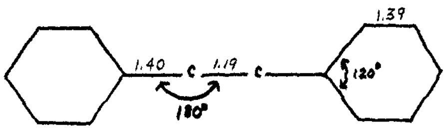


Figure 5.—Bond distances and bond angles in diphenylacetylene.

Table I

Energy of Diphenylacetylene as a Function of the Dihedral Angle

θ, deg	CNDO, −E	INDO, −E
0	106.7907	103.2269
45	106.7914	103.2274
90	106.7918	103.2275

Table II

Energy and Dipole Moment of Bis(3′-fluorophenyl)acetylene as a Function of the Dihedral Angle

		CNDO		INDO	
	θ, deg	−E	μ	−E	μ
Cis coplanar	0	160.7563	2.6 D	154.5744	2.7 D
	90	160.7588	1.9 D	154.5764	1.9 D
Trans coplanar	180	160.7564	0.0 D	154.5745	0.0 D

For the unsubstituted diarylalkyne the barrier to internal rotation is calculated to be 0.0011 h (0.7 kcal/mol) by the CNDO method and 0.0006 h (0.4 kcal/mol) by the INDO method. The two methods are certainly not this accurate; therefore, both can be said to predict a system with virtual free internal rotation. For the difluoro-substituted compound, both approaches predict the perpendicular form to be slightly more stable. The barrier by way of the trans-coplanar transition state is calculated to be 0.0024 h (1.5 kcal/mol) from the CNDO method and 0.0019 h (1.2 kcal/mol) by the INDO method. Again, the barrier is predicted to be quite small.

It is worthwhile to note that the energy of the valence electrons is in all cases calculated to be lower in the coplanar form. It is the core–core repulsions that decrease in passing to the perpendicular geometry, and this decrease compensates almost exactly for the

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(1) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).

(2) J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965).

(3) The program used in these calculations was 141 CNINDO-CNDO and INDO Molecular Orbital Program, L. George, July 22, 1969. The values assigned to the various parameters that occur in the calculations were those in the original program. No values were changed. See also, J. A. Pople and D. L. Beveridge, "Approximate Molecular Theory," McGraw-Hill, New York, N. Y., 1970.

(4) D. R. Lide, *J. Chem. Phys.*, **29**, 1426 (1958).

(5) C. C. Lin and J. D. Swalen, *Rev. Mod. Phys.*, **31**, 841 (1959).

(6) J. M. Robertson and I. Woodward, *Proc. Roy. Soc., Ser. A*, **164**, 436 (1938).

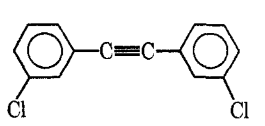
increase in valence–electronic energy. The calculated barriers are small differences between large numbers.

Fortunately, it is possible to obtain experimental evidence for the geometry of diarylalkynes. An X-ray crystallographic study has been made by Robertson and Woodward[6] on diphenylacetylene itself, and the results of this study indicate that the molecule exists in the coplanar geometry with D_{2h} symmetry.[7]

One can, of course, argue that in the solid state lattice packing plays a large role and alters the preferred geometry of the molecule. Certainly, data on the geometry of the molecule in solution are to be preferred. With this end in mind, the ultraviolet spectrum of diphenylacetylene was compared with those of phenylacetylene and *cis-* and *trans*-stilbene.

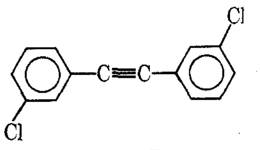
If diphenylacetylene exists in the coplanar form in solution, the chromophore in the near ultraviolet is stilbene-like; see Figure 1. Whereas, if it exists in the perpendicular form, the chromophore is roughly that of two phenylacetylene units (Figure 2). Now the λ_{max} for phenylacetylene occurs at 235 mμ, while those of *cis-* and *trans*-stilbene occur at 280 and 295 mμ, respectively.[8] The spectrum of diphenylacetylene exhibits no peaks between 230 and 260 mμ. A number of peaks are found above 264 mμ with the major ones appearing at 279 and 295 mμ. The chromophore in diphenylacetylene certainly absorbs in the stilbene region, and the spectrum has no peaks at all in the region where phenylacetylene absorbs. Therefore, one may conclude from the ultraviolet data that diphenylacetylene is also coplanar in solution.

A final set of experiments used to find the geometry in solution was the determination of the dipole moment of bis(3′-chlorophenyl)acetylene. This molecule can exist in the cis-coplanar form **3**, the trans-coplanar form **4**, the perpendicular form **5**, or the freely rotating form **6**. The dipole moment in geometries **3**, **4**, and **5** was calculated by the method of vectorial addition of group moments. The dipole moment for the freely rotating case is the root mean square moment, determined by integrating over all values of the dihedral angle.[9]



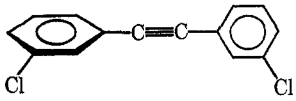
μ = 2.7 D

3



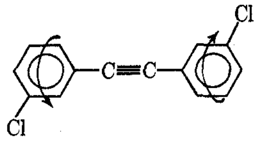
μ = 0.0 D

4



μ = 1.9 D

5



μ = 1.9 D

6

This compound was prepared according to the method of C. D. Weis,[10] and the dipole moment was determined at 20° by measuring the dielectric constants of a series of solutions of the alkyne in carbon tetrachloride.

It is necessary to determine the polarization of the alkyne at infinite dilution and since a direct extrapolation can lead to error, we decided to use an analytic method derived by Hedestrand.[11] The value found in this way was substituted into the Debye equation. The molar refraction of the alkyne was determined by a similar equation, and the value was used to approximate the induced polarization. The dipole moment was calculated to be 1.7 ± 0.1 D. This value does not correspond to any of those just presented but can be explained by assuming that bis(3′-chlorophenyl)acetylene exists in solution in more than a single geometry. The low experimental value of the dipole moment requires, however, that one of the components of the mixture be the trans-coplanar form **4**. We know that some of the molecules must exist in the coplanar form. It is then reasonable to assume that all of them do and that the other component is the cis form **3**. Thus, the dipole moment of the molecule also indicates a coplanar geometry for diarylalkynes.

To summarize, it was found that quantum mechanical calculations, the CNDO and INDO methods, predicted that diarylalkynes existed either with relatively unhindered rotation or with the perpendicular geometry being slightly more stable, approximately 1 kcal/mol. Experimental evidence, on the other hand, does not support these predictions. Three different experimental results indicate a coplanar geometry for diarylalkynes. An X-ray diffraction study showed diphenylacetylene to be coplanar in the solid state while uv spectra afford a similar result for the molecule in solution. The dipole moment of a dichloro derivative seems to confirm the experimental findings.

Experimental Section

The dipole moment of bis(3′-chlorophenyl)acetylene was evaluated at 20° by the method of Hedestrand.[11] According to this method, the dielectric constants and the densities of the solutions are plotted against the mole fractions of the solute. The equations are $\epsilon_s = \epsilon_1 + aX_2$ and $d_s = d_1 + bX_2$. The slopes of the lines, a and b, are substituted into the equation

$$P_2^0 = \frac{\epsilon_1 - 1}{\epsilon_1 + 2}\frac{1}{d_1}\left(M_2 - \frac{M_1 b}{d_1}\right) + \frac{3M_1 a}{(\epsilon_1 + 2)^2 d_1}$$

The subscripts s, 1, and 2 refer to solution, solvent, and solute, respectively.

The value of P_2^0, calculated in this way, is substituted into the equation

$$P_2^0 = \frac{4\pi N\mu^2}{9kT} + R_2^0$$

where R_2^0 is determined by substituting the square of the refractive index n^2 for ϵ in the above equation. The value of a is determined by plotting n_s^2 against X_2. A plot of n_s against X_2 may also be used. The value of a is then twice this slope multiplied by the refractive index of the solvent.

Table III

$X_2 \times 10^2$	2.437	3.283	4.060	4.922	5.814	CCl_4
ϵ_s	2.357	2.400	2.436	2.474	2.514	2.239
d_s	1.576	1.574	1.573	1.566	1.560	1.594

$X_2 \times 10^2$	0.218	0.460	0.676	0.863	1.010	CCl_4
n_s	1.4602	1.4612	1.4622	1.4631	1.4637	1.4592

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[7] "Tables of Interatomic Distances, and Configurations in Molecules and Ions," The Chemical Society, London, 1958, p M239.

[8] G. Riezebos and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **80**, 446 (1961).

[9] J. W. Williams, *Z. Phys. Chem.*, **138**, 75 (1938).

[10] C. D. Weis, *Helv. Chim. Acta*, **49**, 234 (1966).

[11] G. Hedestrand, *Z. Phys. Chem.*, **2**, 428 (1929).

Capacitance measurements were made on a General Radio Model 1620-A capacitance measuring assembly, and refractive indexes were determined using a Brice-Phoenix differential refractometer.

Registry No.—1, 501-65-5; 2, 23349-16-8; bis-(3′-chlorophenyl)acetylene, 5216-30-8.

Acknowledgments.—The authors are indebted to Dr. E. Wagner, Department of Chemistry, Washington State University, for helpful discussions, and to the Schering Corporation and to the Department of Chemistry, Upsala College, for use of their facilities.

The Reaction of Propargyl Alcohols with Halogen Donors. A Novel Phosphorus-Oxygen Heterocycle

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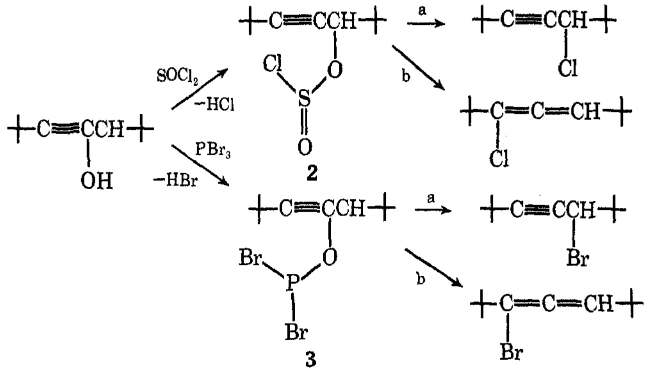
Out attempts to synthesize 1,3-di-*tert*-butyl-1-haloallenes have included an investigation of the reactions of 1,3-di-*tert*-butylpropargyl alcohol (1)[1] with halogen donors such as thionyl chloride and phosphorus tribromide. It is generally believed that reactions of alcohols with these reagents involve intermediate formation of the derived inorganic "ester" (*e.g.*, 2 or 3), which then undergoes intra- or intermolecular attack by halide yielding the substitution product.[2,3] In the case of propargyl alcohols, two pathways are open to the "ester" intermediate: (a) S$_N$i (or S$_N$2) attack at the leaving-group-bearing atom to yield propargyl halide, and (b) S$_N$i′ (or S$_N$2′) attack at C_3 leading to allenic halide.[4]



The reaction of 1 with thionyl chloride led, in 81% yield, to a mixture of the propargyl and allenic chlorides in the ratio 3:1. When 1 was allowed to react with phosphorus tribromide, the expected mixture of propargyl and allenic bromides was obtained (ratio 17:3) in a crude yield of 80%. In addition, however, a significant (*vide infra*) amount of a crystalline solid 4, separable from the liquid bromide product mixture by centrifugation or filtration, was isolated. Compound 4 was purified by recrystallization and sublimation to give stable, colorless crystals, mp 133.2–134.4°. This material reacted rapidly with alcoholic silver nitrate to yield silver bromide. Although it reacted fairly rapidly with aqueous potassium permanganate, 4 reacted only slowly with bromine in carbon tetrachloride at room temperature. The compound was highly soluble in chloroform and methanol, moderately soluble in heptane and ether, and insoluble (*vide infra*) in water.

The mass spectrum of 4 (Table I) confirmed the presence of bromine with pairs of peaks at *m/e* 281, 279; 240, 238; and 225, 223; A relatively intense peak at *m/e* 215 *not* containing bromine suggested parent masses of 294 and 296, and, although these could not be discerned from background, a pair of peaks at *m/e* 295, 297 (M + 1) was observed.[5] The parent masses correspond to a molecular formula $C_{11}H_{20}O_2PBr$, which was confirmed by elemental analysis (see Experimental Section).

TABLE I

PARTIAL 30-eV MASS SPECTRUM OF 4

m/e	Abundance, %	Assignment
297	2	M + H
295	2	
281	7	M − CH_3
279	7	
240	99	M − C_4H_8
238[a]	100	
225	90	M − (C_4H_8 + CH_3)
223	91	
215	73	M − Br
159	60	M − (C_4H_8 + Br)
57	72	$C_4H_9^+$

[a] Base peak.

The infrared spectrum of 4 (chloroform solution) showed weak but sharp absorptions at 3005 (=CH), 1615 (C=C), and 1194 cm^{-1} (P–O–C)[6] and additional intense absorptions at 2960, 1480, 1370, 1310, 1275, 1250, 1073, 1012, 963, 907, 870, 847, 650, 611, 523, and 400 cm^{-1}. Of these, the strongest band at 1250 cm^{-1} could be assigned to P=O.[7] The ultraviolet spectrum (in pentane solution) exhibited relatively intense end absorption extending to 240 nm, with an apparent shoulder at 205 nm (log ϵ 3.90).

The nuclear magnetic resonance spectra (^1H and ^{31}P) were quite interesting. The 90-MHz proton spectrum (deuteriochloroform solution, internal TMS) contained δ 1.03 (s, 9 H), 1.37 (s, 9 H), 4.87 (d of d, J_{P-H_1} = 5.5, $J_{H_1-H_2}$ = 1.8 Hz, 1 H), 6.69 (d of d, J_{P-H_2} = 56.5 Hz, $J_{H_2-H_1}$ = 1.8 Hz, 1 H). Irradiation of the absorption centered at δ 4.87 (H_1) caused the δ 6.69 absorption (H_2) to collapse to a doublet (J_{P-H_2} = 56.5 Hz), confirming the proton-proton coupling scheme. The ^{31}P

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(1) (a) W. T. Borden and E. J. Corey, *Tetrahedron Lett.*, 313 (1969); (b) R. S. Macomber, *ibid.*, 4639 (1970).

(2) J. March, "Advanced Organic Chemistry," McGraw-Hill, New York, N. Y., 1968.

(3) While thionyl chloride generally reacts with an equimolar amount of alcohol, each mole of phosphorus trihalide reacts with 3 mol of alcohol.

(4) For example, see R. J. D. Evans, S. R. Landor, and R. T. Smith, *J. Chem. Soc.*, 1506 (1963).

(5) The appearance of M + 1 peaks where parent ions are absent is not without precedent, especially in oxygenated systems: J. H. Beynon, "Mass Spectrometry and its Application to Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960.

(6) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Top. Phosphorus Chem.*, 5, 317 (1967).

(7) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962.