results. The analytical results were in atoms per cent. deuterium in the compound and were converted into atoms of deuterium per molecule by dividing by 100 and multiplying by the total number of hydrogen and deuterium atoms in the molecule.

Infrared Measurements.—Infrared spectrograms were taken on carbon tetrachloride solutions of all of the organic deuterium compounds used with a Baird double-beam recording infrared spectrophotometer. Table III gives a summary of the bands observed in the C–D stretching region.

A Molecular Orbital Treatment of the Ionization Equilibria of Triarylchloromethanes

BY ANDREW STREITWIESER, JR.[1]

The experimental free energies of ionization of triarylchloromethanes in liquid sulfur dioxide were found to be a smooth function of the increase in resonance energies attending the ionization as calculated by the simple LCAO molecular orbital method.

The correlation of experimental reactivities of π-electron systems with molecular orbital calculations has recently been reviewed by Brown.[2] The simple Linear Combination of Atomic Orbitals (LCAO) molecular orbital method has found qualitative success in the treatment of such systems as orientation in aromatic substitution,[3] relative rates of Diels–Alder reactions[4] and the reaction

Fig. 1.—Shedlovsky plots for α-naphthyldiphenylchloromethane, ●, and β-naphthyldiphenylchloromethane, O, from the data of Ziegler and Wollschitt.[8]

of double bond systems with osmium tetroxide.[3,5]

Unfortunately, there has been a lack of suitable experimental data for quantitative comparison with the results of molecular orbital calculations. However, the recent work of Lichtin and Bartlett[6] and of Lichtin and Glazer[7] provides an excellent opportunity for an experimental test: these authors measured the extent of ionization of triarylchloromethanes in liquid sulfur dioxide, expressing their results in terms of an experimental free energy. While these free energy values are not those of the true equilibrium, $R_3CCl \rightleftarrows R_3C^+ + Cl^-$, because of significant ion-pair association, the dissociation of the ion pairs is approximately constant for a related series of compounds and the experimental free energies are quantitative measures of the tendency of the triarylchloromethanes to ionize. Among the compounds measured, those which are amenable to simple LCAO calculation are triphenylchloromethane and its mono-m-phenyl and mono-p-phenyl derivatives. In addition, the earlier data of Ziegler and Wollschitt[8] were used to calculate the experimental free energies for di-p-biphenylylphenyl-,[7] tri-p-biphenylyl-[7] and tri-m-biphenylylchloromethanes.[9] The data of Ziegler and Wollschitt were used to construct Shedlovsky plots for α-naphthyldiphenylchloromethane and β-naphthyldiphenylchloromethane in the manner detailed by Lichtin and Bartlett.[6] The second approximation Shedlovsky plots for these compounds are reproduced in Fig. 1. All of the experimental free energies (ΔF) are listed in Table I.

Because of its extended conjugated system, a triarylmethyl cation possesses greater resonance energy than its derived chloride. One would expect, a priori, that as this difference in resonance energy increased, the extent of ionization would increase and that the experimental free energy
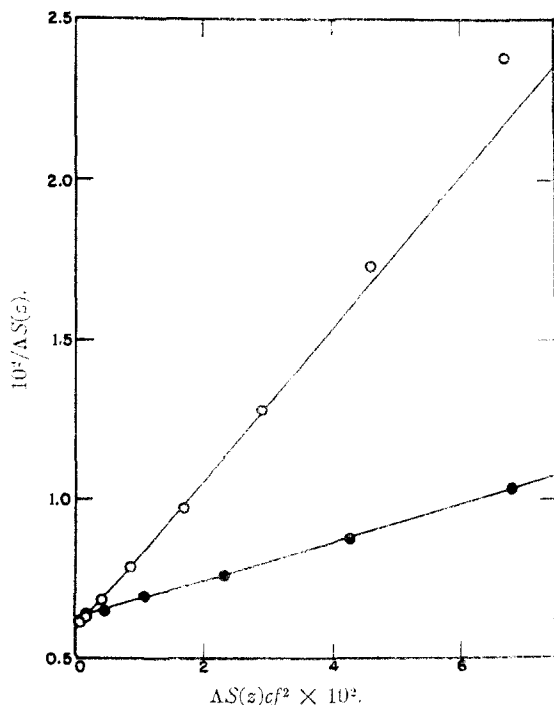
(1) U. S. Atomic Energy Commission Post-doctoral Fellow, 1951–1952. Department of Chemistry, University of California, Berkeley 4, Calif.

(2) R. D. Brown, *Quart. Rev.*, **6**, 63 (1952).

(3) G. W. Wheland, THIS JOURNAL, **64**, 900 (1942); J. D. Roberts and A. Streitwieser, J., *ibid.*, **74**, 4723 (1952).

(4) R. D. Brown, *J. Chem. Soc.*, 691 (1950), 3129 (1951).

(5) R. D. Brown, *ibid.*, 3249 (1950).

(6) N. N. Lichtin and P. D. Bartlett, THIS JOURNAL, **73**, 5530 (1951).

(7) N. N. Lichtin and H. Glazer, *ibid.*, **73**, 5537 (1951).

(8) K. Ziegler and H. Wollschitt, *Ann.*, **479**, 108 (1930).

(9) Private communication from N. N. Lichtin.

TABLE I

EXPERIMENTAL FREE ENERGIES AND CALCULATED RESONANCE ENERGIES OF IONIZATION IN LIQUID SULFUR DIOXIDE

	R1	R2	R4	DE of chloride[a,b]	DE of carbonium ion[b]	ΔDE[b]	ΔF,[c] kcal.-mole^{-1}	δ[d]
A	H	H	H	6.0000	7.8004	1.8004	5.49[e]	0.308
B	H	H	m-C6H5	8.3834	10.1824	1.7990	5.61[f,g]	.308
C	m-C6H5	m-C6H5	m-C6H5	13.1502	14.9462	1.7960	6.07[h]	.308
D	H	H	p-C6H5	8.3834	10.2018	1.8184	4.54[f]	.291
E	H	p-C6H5	p-C6H5	10.7668	12.6064	1.8396	3.75[f]	.276
F	p-C6H5	p-C6H5	p-C6H5	13.1502	15.0080	1.8578	3.17[f]	.262
G	α-Naphthyldiphenylmethyl			7.6832	9.5376	1.8544	3.96[i]	.290[j]
H	β-Naphthyldiphenylmethyl			7.6832	9.4966	1.8134	4.80[i]	.295[i]

(Column header structure at top left: R1—C6H4, R2—C6H4, R3—C6H4 forming >C— with R2 shown below.)
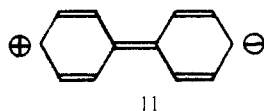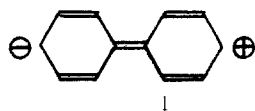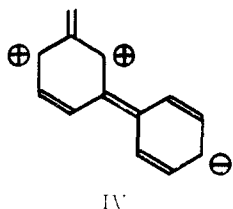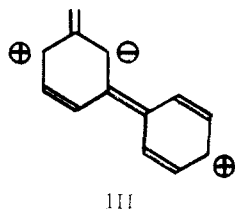
[a] Computed as the sum of the resonance energies of the constituent aromatic rings. Values computed for the DE's are: benzene, 2.0000 β; biphenyl, 4.3834 β; naphthalene, 3.3832 β. [b] In terms of β. [c] At 0.0–0.1°. [d] Positive charge density on the methyl carbon in the carbonium ion. See appendix. [e] Ref. 6. [f] Ref. 7. [g] The value 5.63 given by Lichtin and Glazer[7] contains an arithmetic error (private communication from Dr. N. N. Lichtin). [h] Ref. 9. [i] This paper from data of Ziegler and Wollschitt.[8] [j] The method outlined in the appendix is inapplicable to naphthyl systems; cf. Ref. 16.

would decrease. The extent to which the free energies are a quantitative function of this difference in resonance energies was determined by the simple LCAO method.

Results and Discussion

The calculations were carried out in the usual manner[10] with orthogonal orbitals. The approximation of setting $S = 0$ affects the absolute values of the π-electron energies, but does not appreciably change their relative values which are all that is required for comparison purposes. The calculated delocalization (resonance) energies (DE) of each of the above triarylmethyl chlorides and carbonium ions and the differences (ΔDE) between these quantities are given in Table I in terms of the exchange integral, β.

The validity of the LCAO method has been the subject of some discussion.[11] One basic requirement for validity is the assumption of a self-consistent field.[11b] For alternant[11b] hydrocarbons this requirement is fulfilled and for such systems the LCAO approximation is considered to be quite good.[12] It is not known to what extent the approximation suffers when applied to systems such as the carbonium ions treated in the present paper which do not have self-consistent fields but it seems probable that at least the relative values obtained are meaningful. This limitation must, however, be kept in mind in the discussion which follows.

When the experimental free energies are plotted against the differences in calculated resonance energies (Fig. 2), seven points define a remarkably smooth curve indicating that the extent of ionization is a function of the change in resonance energy upon dissociation. That this function is not linear may be due to any one or more of the limitations discussed above, or to the fact that the experimental quantity is free energy while the calculations consider only energy, the entropy of reaction being neglected.

(10) C. A. Coulson and H. C. Longuet-Higgins, Proc. Royal Soc. (London), 191, 39 (1947); cf. also B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson et Cie, Paris, 1952, p. 176.

(11) (a) G. W. Wheland, J. Chem. Phys., 2, 474 (1934); (b) C. A. Coulson and G. S. Rushbrooke, Proc. Cambridge Phil. Soc., 36, 193 (1940).

(12) This is apparently true only for aromatic hydrocarbons; cf. D. P. Craig, J. Chem. Soc., 3175 (1951).

Fig. 2.—Correlation curve of experimental ionization free energies (ΔF) and LCAO resonance energy differences (ΔDE). Letters refer to compounds in Table I.

As expected, p-phenyl substituents increase the resonance energy of the tritylcarbonium ion, giving considerable enhancement to ionization. More interesting is the effect of meta substitution. The calculations demonstrate that a m-phenyl substituent increases the resonance energy of trityl chloride more than it increases that of the carbonium ion. That the ionization of m-phenyltriphenylmethyl chloride is accompanied by a smaller increase in resonance energy than is the ionization of trityl chloride itself is consistent with the observed increase in ΔF with the meta-substituted compound. This result may perhaps be visualized by a consideration of some of the valence-bond canonical structures.[13] Part of the resonance of biphenyl stems from structures such as I and II.

(13) It should be noted that this valence-bond analogy is not an exact one; however, the valence-bond method often has the advantage of yielding results that may be visualized in a pictorial sense and this analogy is given here only to indicate in a manner easily visualized how the same result for the m-phenyl compounds could result from application of the valence-bond method.

Considering the similar structures, III and IV,

contributing to the resonance energy of a *m*-phenylbenzyl cation, the contribution of III would be expected to be comparable to that of I, but structure IV, possessing two like charges in one ring, would contribute much less than II. The over-all result would therefore be a decrease in the contribution of the charge-separated structures in the *m*-phenyl case; *i.e.*, a *m*-phenyl substituent stabilizes an uncharged ring more than it does a charged one. These considerations also rationalize the electronic influence of *m*-phenyl groups in other systems. A consequence[14] of this interpretation is that *m*-biphenylyldiphenylmethane should be less acidic than triphenylmethane in contrast to the increase in acidity expected if a *m*-phenyl substituent is intrinsically electron-attracting.[7] Experiments designed to test this point are planned.

Also interesting are the naphthyl systems. The planar β-naphthyldiphenylmethylcarbonium ion is no more sterically hindered than is trityl-carbonium ion but Fisher–Hirschfelder–Taylor models demonstrate that α-naphthyldiphenylmethylcarbonium ion is so sterically hindered that the three groups must be distorted considerably from a coplanar configuration. These considerations are consistent with the observation that the β-naphthyl point falls on the curve in Fig. 2 while the α-naphthyl system is considerably displaced; *i.e.*, α-naphthyldiphenylchloromethane ionizes to a smaller extent than is predicted on the basis of a planar carbonium ion. It should be noted that none of the triarylmethylcarbonium ions is strictly coplanar; *i.e.*, the aromatic rings are twisted slightly out of the plane by ortho-hydrogen repulsion.[15] The extent of this distortion would

(14) In the LCAO method, ions of the type treated in this paper possess one orbital of zero bonding energy. This orbital, empty for the cations, contains two electrons for the corresponding anions. Thus, the *DE*'s of the anions are the same as those of the cations and the ΔDE's listed in Table I will also apply to the production of the anions from the corresponding hydrocarbons; therefore, a decrease in ΔDE should be associated with a decrease in the acidity of the hydro-carbon if the same type of correlation curve applies.

(15) C. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 187; however, for an extreme

not be appreciably affected by meta- or para substitution and is, therefore, a relatively constant factor in the above series, but would be considerably increased by ortho substitution.

The success of the simple LCAO method in this system is such that the correlation curve obtained could very probably be used to determine the extents of ionization of as yet experimentally un-investigated similar triarylchloromethanes.

Appendix

Electron Densities.—In the course of this work electron densities were calculated for the carbonium ions and a general method was inductively established[16] for determining these by inspection. In this method, which can be applied to any methyl cation substituted by any number of phenyl rings, if the charge on the central carbon is δ, then the charge of any adjacent phenyl group is $^3/_4 \delta$, divided equally among the o- and p-positions. The adjacent carbon and the m-positions bear none of the charge. Similarly, any other phenyl group bears an amount of charge $^3/_4$ that of the carbon atom to which it is attached. Since the summation of the charge over all the carbon atoms must equal unity, δ is easily found. As an illustration of the application of the method, p-phenylbenzylcarbonium ion (V) has the charge densities shown, from which it follows that $\dfrac{31}{16} \delta = 1$ and that $\delta = 0.516$. The values of δ for the carbonium ions treated in this paper are given in the last column of Table I.

V
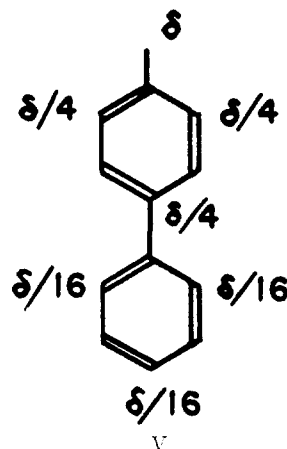
An analogous procedure, may, of course, be used with the corresponding anions.

CAMBRIDGE, MASSACHUSETTS

view see M. S. Newman and N. C. Deno, THIS JOURNAL, **73**, 3644 (1951).

(16) A more general method was proved by H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 278 (1950).