after 15 ml of absolute ethanol was added with thorough stirring. Solvents were removed and the residue was separated from a column of silica gel (15 × 0.5 in.). The carbamate **4a** was eluted with 900 ml of a 1:1 mixture of *n*-hexane and benzene; after removal of solvent, sublimation at 40° (0.4 mm) gave 3.16 g (39.2%) of a colorless powder, mp 78–79.5° dec, identical by melting point and ir comparison with an authentic sample prepared from cyclohexyl isocyanate and *tert*-butyl alcohol, ir ($CHCl_3$) 3470 (NH), 1705 (CO), and 1510 cm^{-1} (secondary amide). Next the chlorocyclohexylcarbamate **6** was eluted with 300 ml of a 1:2 mixture of *n*-hexane and benzene; after removal of solvent, sublimation at 80° (0.4 mm) gave 112 mg (1.2%) of a colorless powder: mp 124–125.5°; ir ($CHCl_3$) 3450 (NH), 1705 (CO), and 1495 cm^{-1} (secondary amide). *Anal.* Calcd for $C_{11}H_{20}NO_2Cl$: C, 56.52; H, 8.62; N, 5.99; Cl, 15.16. Found: C, 56.31; H, 8.71; N, 5.82; Cl, 15.47.

A third component was eluted with 300 ml of chloroform; after removal of solvent, sublimation at 40° (0.4 mm) gave 0.11 g (2.1%) of *tert*-butyl carbamate as colorless needles, mp 106–108°. Finally 600 ml of 95% ethanol removed cyclohexylamine hydrochloride; after removal of solvent, sublimation at 120° (0.4 mm) gave 1.26 g (21.1%) of a colorless powder, mp 204° dec. Both *tert*-butyl carbamate and cyclohexylamine hydrochloride were identical with authentic samples.

In a similar reaction between benzhydryl isocyanate and *tert*-butyl hypochlorite (in a molar excess) without a solvent at 70°, the ester **5b** was isolated by sublimation at 85° (0.4 mm) in 87% yield: ir ($CHCl_3$) 1725 (CO) and 1625 cm^{-1} (C=N); nmr ($CDCl_3$) δ 7.5 (s, 10, C_6H_5), 1.3 [s, 9, $(CH_3)_3C$]; mass spectrum (70 eV) *m/e* 281 (M^+). *Anal.* Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.97; mol wt, 281.36. Found: C, 76.58; H, 6.83; N, 4.94. Hydrolysis gave *tert*-butyl carbamate and benzophenone, identified by comparison with authentic data. Decomposition resulted from heating in a sealed melting point tube at 180° for 2 hr. Dissolving the combined residues from six tubes containing a total of 56 mg of **5b** in petroleum ether which was then saturated with a stream of anhydrous hydrogen chloride gave 25 mg (57%) of the hydrochloride of the imine of benzophenone, sublimation point 250°,[6] ir absorption identical with an authentic spectrum.

From phenyl isocyanate and *tert*-butyl hypochlorite in equimolar portions in petroleum ether at room temperature *o*- (**7**) and *p*-chlorophenylcarbamate (**8**) were obtained by elution from silica gel with hexane. The ortho isomer separated first, 1.7 g (17.7%) after distillation at 120–122° (0.4 mm). Redistillation gave a yellow liquid with constant $n^{25}{}_{D}$ 1.5231; ir ($CHCl_3$) 3420, 1725, and 1510 cm^{-1}; nmr ($CDCl_3$) δ 8.37–8.22 (br, 1, NH), 7.32 (m, 4, C_6H_4), 1.52 [s, 9, $(CH_3)_3C$]; mass spectrum (70 eV) *m/e* 227 (M^+). *Anal.* Calcd for $C_{11}H_{14}NO_2Cl$: C, 58.02; H, 6.19; N, 6.15; Cl, 15.57; mol wt, 227.69. Found: C, 57.82; H, 6.16; N, 6.12; Cl, 15.55.

The para isomer **8** sublimed at 80° (0.4 mm) and gave 2.27 g (23.5%) of a colorless powder, mp 95–99°, which recrystallized from *n*-heptane as needles: mp 102–104°; ir ($CHCl_3$) 3420, 1725, and 1510 cm^{-1}; nmr ($CDCl_3$) δ 7.28 (m, 4, C_6H_4), 6.7 (br, 1, NH), 1.5 (s, 9, $(CH_3)_3C$]; mass spectrum (70 eV) *m/e* 227 (M^+). Chloroform eluted *N,N'*-diphenylurea identified by comparison with authentic data.

Registry No.—**2**, 507-40-4; **4a**, 3712-40-1; **5b**, 35426-67-6; **6**, 35426-68-7; **7**, 35426-69-8; **8**, 18437-66-6.

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Anomalous Properties of Halogen Substituents

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The electron-attracting tendencies of halogen substituents in aliphatic compounds are well established, on the basis of such familiar evidence as the increase in the acidity of carboxylic acids[1] and many other organic compounds[2,3] upon substitution by halogens. A quantitative measure of this "inductive effect" is the substituent constant σ_I.[4,5] The values of σ_I for the halogens are given in Table I; as anticipated, they show the same trend as the electronegativities of these elements.

TABLE I

HALOGEN ELECTRONEGATIVITIES AND SUBSTITUENT CONSTANTS

Halogen	Electronegativity[a]	σ_I[b,c]	σ_R[b,c]
F	4.0	+0.51	−0.34
Cl	3.0	+0.47	−0.20
Br	2.8	+0.45	−0.16
I	2.5	+0.39	−0.12

[a] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960. [b] P. R. Wells, S. Ehrenson, and R. W. Taft, in "Progress in Physical Organic Chemistry," Vol. 6, A. Streitwieser and R. W. Taft, Ed., Interscience, New York, N. Y., 1968. [c] The more positive the value of σ_I, the greater is the electron-attracting tendency; the more negative the value of σ_R, the greater is the electron-donating tendency.

These electron-attracting powers are presumably also operative when the halogens are substituents on aromatic rings; indeed, the halobenzenes are less reactive toward electrophilic attack than is benzene.[6] However, substituents which simply withdraw electrons from the ring are found to be meta directing,[7] whereas the halogens are ortho and para directing.[6,7] This is generally interpreted as indicating a concomitant donation, or feedback, of electrons to the ring by the halogen substituent,[7,8] and is usually described as a "resonance effect." Surprisingly, this supposed electron-donating tendency increases in the order I < Br < Cl < F; the greatest feedback seems to occur when the substituent is fluorine, the most electronegative element. For instance, fluorine deactivates a benzene ring less than does chlorine,[6] and in fact, using partial rate factors, some electrophilic substitutions are found to occur more rapidly at the para position in fluorobenzene than at any single position in benzene. Relatively stable protonated fluorobenzenes have even been observed.[9] The extent of this "resonance effect" is measured by another substituent constant, σ_R (Table I).[10]

The trend in the supposed electron-donating powers, as indicated by the σ_R values, and especially the be-

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(1) See, for example, R. T. Morrison and R. N. Boyd, "Organic Chemistry," 2nd ed, Allyn and Bacon, Boston, Mass., 1966.

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(7) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969.

(8) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969. This book gives an excellent review of many of the points discussed in this paper.

(9) G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **89**, 5692 (1967).

(10) R. W. Taft and I. C. Lewis, *ibid.*, **81**, 5343 (1959); R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 3146 (1963).

Table II

Values of Overlap and Repulsion Integrals

Halogen, X	C–X bond length,[a] Å	Overlap values		$R_{\pi C-\pi X}$	$R_{\pi C-\sigma X}$	$R_{\sigma C-\pi X}$	$R_{\sigma C-\sigma X}$
		Slater-type orbitals	Cusachs–Corrington orbitals				
F	1.328	0.146	0.217	0.353	0.373	0.422	0.457
Cl	1.70	0.166	0.230	0.279	0.315	0.309	0.361
Br	1.85	0.152	0.225	0.256	0.296	0.279	0.334
I	2.05	0.138	0.207	0.231	0.275	0.246	0.304

[a] These are the average C–X bond lengths for halogens substituted on aromatic rings, as given in "Tables of Interatomic Distances and Configuration in Molecules and Ions," Supplement, L. E. Sutton, Ed., Special Publication No. 18, The Chemical Society, London, 1965.

havior of fluorine, are commonly explained in terms of overlap considerations.[8,11–13] It is argued that the extent of electron back-donation depends upon the degree of overlap between the filled outer pπ orbitals of the halogen and the 2p$_\pi$ orbitals of the aromatic ring carbon to which it is bonded. This overlap, it is claimed, should decrease in the order F > Cl > Br > I, due to the increasing carbon–halogen bond length and the increasing disparity between the sizes of the carbon and the halogen pπ orbitals. Since the C–F bond is by far the shortest of the four (Table II), and since the p$_\pi$ orbitals of fluorine are supposedly the most similar to those of carbon, the overlap, and hence the feedback of electrons, should be greatest in the case of fluorine.

In order to test this interpretation, we have evaluated the relevant overlap integrals, $\int(2p_{\pi C})(np_{\pi X})d\tau$, where $n = 2, 3, 4, 5$ and X = F, Cl, Br, I. Using Slater-type atomic orbitals with the optimized exponents of Clementi and Raimondi,[14] and taking the C–X bond lengths to be the average values for the respective halogens substituted on aromatic rings (Table II), the overlap values listed in column 3 of Table II were obtained.[15]

The results certainly do not support the overlap and back-donation theory. Not only are all four overlap values remarkably similar, but the C–F value, which the theory predicts to be very much the largest, is in fact *smaller* than both the C–Cl and the C–Br values! There is clearly no correlation between degree of overlap and σ_R.

To confirm these results, the overlap integrals were determined for another set of atomic orbitals, the Cusachs–Corrington "overlap-matched" orbitals, which are designed to reproduce as well as possible the overlaps of extended-basis-set self-consistent-field atomic orbitals.[16] The values obtained (Table II, column 4) are slightly different from the previous ones, as is to be expected when using a different set of atomic orbitals, but the same trend is observed. The key C–F overlap is again completely at variance with the theory. It is evident, therefore, that some factor other than overlap and back-donation is responsible for the observed trend in the halogen σ_R values.

It has been suggested that this factor is a repulsive interaction between the outer p$_\pi$ electrons of the halogen and the 2pπ electrons of the aromatic ring, especially those associated with the carbon on which the halogen is substituted.[17–19] This repulsion has the effect of pushing the aromatic π electrons away from the substituted position and into the ring, and will lead to some buildup of π charge at the ortho and para positions.[17,20]

If these repulsive interactions are indeed of such key importance, then there should be a correlation between the coulomb integrals

$$R_{\pi C-\pi X} = \int 2p_{\pi C}(1)2p_{\pi C}(1)\frac{1}{r_{12}}np_{\pi X}(2)np_{\pi X}(2)d\tau_1 d\tau_2$$

and the substituent constants σ_R. The indicated integral is equal to the coulombic energy of repulsion between an electron in a 2p$_\pi$ orbital of carbon and one in an np$_\pi$ orbital of atom X. These integrals were evaluated, using the Slater-type atomic orbitals mentioned earlier, and their values are in column 5 of Table II.[21] The results show the desired trend: $R_{\pi C-\pi F} \gg R_{\pi C-\pi Cl} > R_{\pi C-\pi Br}, > R_{\pi C-\pi I}$. The relationship of these integral values to the substituent constants σ_R is examined more precisely in Figure 1, and the correlation is found to be excellent. A nearly exact linear relationship exists between the repulsion integrals, $R_{\pi C-\pi X}$, and the corresponding σ_R values. This is strong support for the resulsion theory.

While the experimentally observed effects which the present discussion has sought to explain probably involve primarily π electron interactions, a similar line of reasoning can help to elucidate certain rather puzzling

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(11) J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, "Valence Theory," Wiley, New York, N. Y., 1965.

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(13) J. B. Hendrickson, D. J. Cram, and G. S. Hammond, "Organic Chemistry," 3rd ed, McGraw-Hill, New York, N. Y., 1970.

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(15) E. A. Boudreaux, L. C. Cusachs, and L. D. Dureau, "Numerical Tables of Two-Center Overlap Integrals," W. A. Benjamin, New York, N. Y., 1970.

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(17) D. T. Clark, J. N. Murrell, and J. M. Tedder, *J. Chem. Soc.*, 1250 (1963).

(18) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Wiley, New York, N. Y., 1963.

(19) An interesting quantitative treatment of halogen substituent effects, which also emphasizes the importance of repulsive interactions, has been given by D. P. Craig and G. Doggett, *Mol. Phys.*, **8**, 485 (1964).

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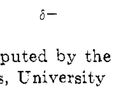

(21) The integrals were computed by the Electronic Structure Software Center, Department of Physics, University of Utah, through the courtesy of Professor Frank E. Harris.

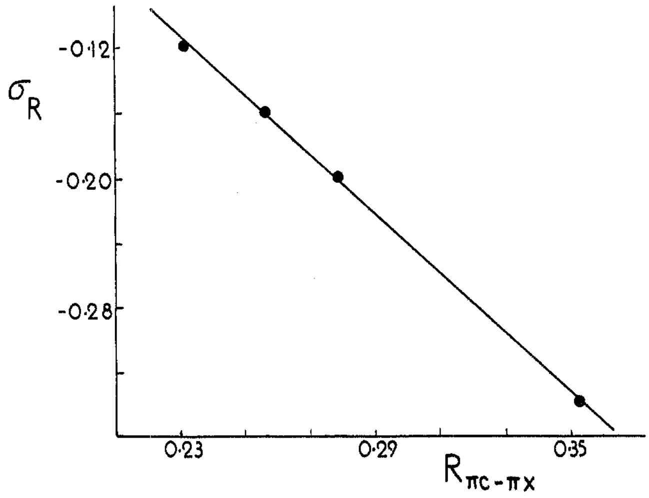

Figure 1.—Relationship between the halogen substituent constants σ_R and the repulsion integrals $R_{\pi C-\pi X}$, where X = F, Cl, Br, I. The repulsion integrals are given in atomic units (1 au = 627.2 kcal/mol).

features of some nonaromatic systems. It has already been shown that several anomalous properties of fluorine, both as a free atom and also in various inorganic and aliphatic compounds, can be explained in terms of the exceptionally strong repulsive force exerted by the fluorine atom's electrons upon any approaching electron.[22] Another interesting anomaly is the fact that the localization of the negative charge in the trihaloacetate and the trihalomethide anions appears to increase as the halogen changes from bromine to fluorine.[23,24] The least delocalization occurs with fluorine, despite its being the most electronegative. Again, this can be interpreted as the result of a very strong repulsive interaction between the fluorine electrons and the negative charge, an interaction which diminishes markedly in going on to chlorine and bromine. In columns 6–8 of Table II are presented the values of three more types of coulomb repulsion integrals: $R_{\pi C-\pi X}$, $R_{\sigma C-\pi X}$, and $R_{\sigma C-\sigma X}$.[21] These integrals represent the other possible combinations of p_π and p_σ orbitals on the carbon and the halogen atoms; they are defined analogously to $R_{\pi C-\pi X}$. In each case, the same trend is observed as before: $R_{C-F} \gg R_{C-Cl} > R_{C-Br} > R_{C-I}$. Thus, whether any given situation of interest involves primarily one of these types of interaction or, as is more likely, two or more of them simultaneously, it is evident that a consideration of electronic repulsion interactions will help to explain many of the seemingly anomalous properties of the halogens, and of fluorine in particular.

Registry No.—F, 16984-48-8; Cl, 16887-00-6; Br, 24959-67-9; I, 20461-54-5.

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[23] J. Hine and N. W. Burske, *ibid.*, **78**, 3337 (1956).

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Synthesis and Reactivity of 2,2'-Bis(phenylethynyl)diphenylacetylene

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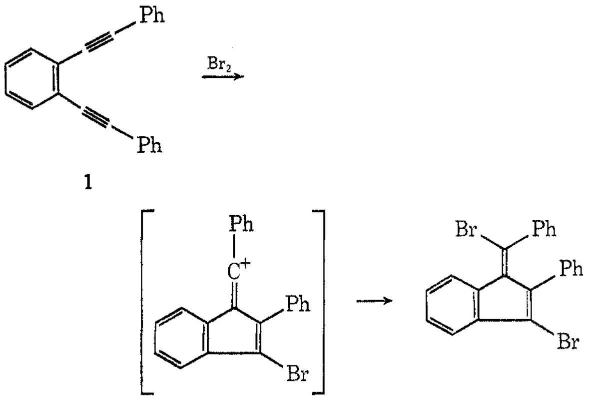
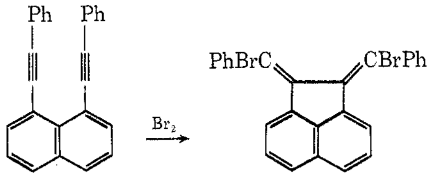
Interaction between spatially proximal acetylenic groups on chemical reaction has been demonstrated.[1-6] This occurs even if there is little angle strain to be relieved on addition of reagents (eq 1[1] and 2[5]). Evidence for the concerted nature of acetylene–acetylene interaction following attack of electrophilic reagents on **1** has been presented.[1] The type of ring system produced by addition of reagents to oligoacetylenes of this type must be at least partially dependent on the geometrical disposition of the triple bonds relative to one another. On consideration of the above results we have been prompted to synthesize the title triyne **2** to see whether it is attacked by electrophilic reagents in a manner analogous to **1**. This is observed (Scheme I).



(1)



(2)

Results

The reaction of **2** with controlled amounts of bromine affords, in addition to starting material, a mixture of di- and tetrabromides. Chromatography of the hexane-soluble portion of the reaction product afforded an oily dibromide that is assigned the gross structure **3**

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