2.08 (3 H, s, SeCH$_3$), 2.93 (2 H, AB q, δ_{AB} = 22.5 Hz, J_{AB} = 12 Hz, CH$_2$SeCH$_3$), 6.6–7.0 (2 H, m, C-1, C-2H); mass spectrum, *m/e* 398 (M$^+$(^{80}Se)), 396 (M$^+$(^{78}Se)).

3-Acetoxy-16α-iodoestra-1,3,5(10)-trien-17-one (14c). This compound was prepared as described by Mueller and Johns[7] and showed the following: mp 143–144 °C (lit.[7] mp 142–143.6 °C); ^{1}H NMR δ 1.03 (3 H, s, 18-H), 2.3 (3 H, s, 3-OAc), 4.92 (1 H, m, 16β-H), 6.86 (s, C-4H), 6.94 (d, *J* = 2 Hz, C-2H), 7.3 (d, *J* = 9 Hz, C-1H).

3-Acetoxy-16β-fluoroestra-1,3,5(10)-trien-17-one (14d). A mixture of 3-acetoxy-16α-iodoestrone 14c (1 g, 2.37 mmol, 40 mL) and anhydrous silver fluoride (2.8 g, 22 mmol) in dry acetonitrile was refluxed for 3 h and allowed to stand at room temperature for 3 days. The mixture was heated to boiling and filtered. The cooled filtrate was diluted with ether, washed, dried, and evaporated. The resulting brown gum (0.76 g) was dissolved in acetic anhydride (10 mL), refluxed (30 min), and then concentrated in vacuo. The residue was resolved by preparative TLC (same system as above) to give 14c and 3-acetoxy-16β-fluoroestra-1,3,5(10)-trien-17-one (14d, 10%): mp 181–183 °C (182–184 °C); ^{1}H NMR δ 1.03 (3 H, s, 18-H), 2.27 (3 H, s, 3-OAc), 4.7 (1 H, tt, J_1 = 50 Hz, J_2 = 8 Hz, 16α-H), 6.86 (s, C-4H), 6.94 (d, *J* = 3 Hz, C-2-H), 7.3 (d, *J* = 9 Hz, C-1H); mass spectrum, *m/e* 330 (M$^+$), 287 (M$^+$ – CH$_3$COOH).

16β-Fluoroestra-1,3,5(10)-triene-3,17β-diol (15a). A solution of 3-acetoxy-16β-fluoroestrone 14d (50 mg) in absolute ethanol (25 mL) was treated with sodium borohydride (25 mg) at 4 °C for 24 h. The mixture was diluted with water, neutralized with 1% H$_2$SO$_4$, extracted with ethyl acetate, and processed in the conventional manner to give a greyish solid. This was fractionated by TLC (hexane–ethyl acetate (2:1)] to yield 16β-fluoroestradiol 15a (80%): mp 220–223 °C (from methanol); ^{1}H NMR δ 0.85 (s, 3 H, 18-H), 3.43 (1 H, dd, J_1 = 21 Hz, J_2 = 6 Hz, 17α-H), 4.97 (1 H, mm, *J* = 57 Hz, 16α-H), 6.62 (1 H, s, 4-H), 6.7 (1 H, d, *J* = 3 Hz, 2-H), 7.13 (1 H, d, *J* = 8 Hz, 1-H); mass spectrum, *m/e* 290 (M$^+$), 270 (M$^+$ – HF).

Reaction of 3-(Tetrahydropyran-2′-yloxy)estrone Enol Lithium 16 with Perchloryl Fluoride.[8] To a stirred (under argon) suspension of lithium diisopropylamide (302 mg, 2.82 mmol) in dry toluene (4 mL) was added dropwise a solution of

estrone 3-THP ether (1 g, 2.82 mmol) in toluene (6 mL). The resulting yellowish-brown solution was concentrated to one-third of its original volume and dry THF (8 mL) added. Perchloryl fluoride was bubbled through the solution for 2 min at 0 °C. Excess perchloryl fluoride was then removed under reduced pressure (10 min), and the reaction mixture was poured into ice water (100 mL). The product was recovered with ether and processed in the conventional manner to give a gummy residue. Analytical TLC [silica gel, hexane–ethyl acetate (2:1)] indicated the presence of the starting material and of two more products. The THP moiety was cleaved [ethanol (3 mL), 0.4 M H$_2$SO$_4$ (1 mL), 70 °C, 20 min], and the resulting products were resolved by preparative TLC [silica gel, hexane–ethyl acetate (3:1)] to give estrone and 4-chloro-16α-fluoroestrone 17a (50 mg): mp 140–143 °C; ^{1}H NMR δ 0.97 (3 H, s, 18-H), 5.13 (1 H, tt, J_1 = 54 Hz, J_2 = 6 Hz, 16β-H), 6.88 (1 H, d, *J* = 9 Hz, 2-H), 7.18 (1 H, d, *J* = 9 Hz, 1-H); mass spectrum, *m/e* 324, 322 (M$^+$ ions).

4-Chloro-16α-fluoroestra-1,3,5(10)-triene-3,17β-diol (17b). A solution of 4-chloro-16α-fluoroestrone 17a (20 mg) in absolute ethanol (2 mL) was treated with NaBH$_4$ (10 mg) at 4 °C for 24 h. The mixture was diluted with water, neutralized with 1% H$_2$SO$_4$, and then extracted with ethyl acetate. The extract was washed, dried, and concentrated to give 4-chloro-16α-fluoroestradiol 17b as a crystalline residue. The residue was purified by HPLC; mp 162–164 °C; ^{1}H NMR δ 0.81 (3 H, s, 18-H), 2.85 (1 H, dd, J_1 = 285 Hz, J_2 = 5 Hz, 17α-H), 4.97 (1 H, mm, *J* = 55.5 Hz, 16β-H), 6.85 (1 H, d, *J* = 9 Hz, 2-H), 7.16 (1 H, d, *J* = 9 Hz, 1-H); mass spectrum, *m/e* 324, 326 (M$^+$ ions), 304, 306 (M – HF).

Quantitative Description of Steric and Electrical Effects of Planar π-Bonded Groups. 1. Variation of Dihedral Angle with the Size of an Adjacent Group

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The equation 1/sin θ = a_{30}/$\sum r$ + a_{11}, where θ is the dihedral angle and $\sum r$ the sum of the van der Waals r_V of a planar π-bonded substituent (Xpπ) and a nonplanar substituent (Xnp), has been derived. In this relationship, a_{30} is the slope and a_{11} the intercept. Data for 15 sets of compounds in which Xpπ and Xnp are vicinally bonded to a planar π-bonded skeletal group, G, have been correlated with this equation, generally with good results. In some cases, however, best results are obtained with the inclusions of a term for electrical effects in the correlation equation. These results are applicable to a wide range of Xpπ groups, including Ph, CH=CH$_2$, XC$_6$H$_4$, CONH$_2$, CO$_2$H, Ac, and NO$_2$, and to both ortho-substituted benzene and *cis*-vinylene skeletal groups.

It has been shown that the effect of ortho substituents on chemical reactivity or physical properties is well represented by the LDS equation (eq 1), where Q_X is the

$$Q_X = L\sigma_{IX} + D\sigma_{DX} + Sv_X + h \qquad (1)$$

quantity of interest (pK_a, log *k*, μ, v_{CO}, δ_H, etc.), σ_I and σ_D represent the localized (field and/or inductive) and delocalized (resonance) electrical effects. Available σ_D constants include σ_R, σ_R^+, σ_R^-, and σ_R°, the choice depending

on whether or not π delocalization involving the substituent X, the active site Y, and the skeletal group G (to which X and Y are bonded) is possible and on the electronic demand of Y. *v* is a steric parameter based on r_{VX}, the van der Walls radius of X ($v \equiv v_{vx} - 1.20$).

Planar π-Bonded Groups. The inclusion of planar π-bonded substituents, Xpπ, in a data set which is to be correlated with the LDS equation is difficult if a significant steric effect is present. Planar π-bonded groups have the
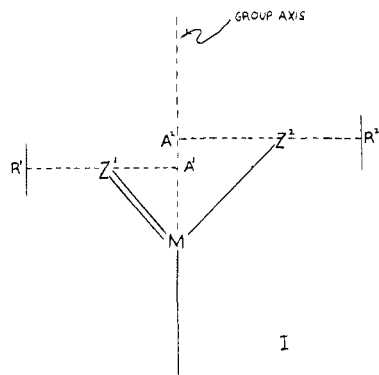
Figure 1. Type I Xpπ group. Only M and Z^1 are π bonded. Distances: $A^1Z^1 = d^1$, $A^2Z^2 = d^2$, $R^1Z^1 = r_{VZ^1}$, $R^2Z^2 = r_{VZ^2}$. $v^1_{max} = d^1 + r_{VZ^1} - 1.20$ and $v^2_{max} = d^2 + r_{VZ^2} - 1.20$.
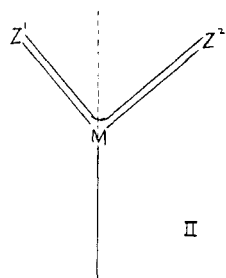

Figure 2. Type II Xpπ group. M, Z^1, and Z^2 are π bonded.

structures, I and II shown in Figures 1 and 2, with Z^1, M, and Z^2 being coplanar. In type I planar π-bonded groups only M and Z^1 are involved in π bonding. In type II planar π-bonded groups, Z^1, Z^2, and M are all involved in π bonding. Examples such as OAc can be considered as type I groups in which Z^2 is a lone pair on oxygen. Examples of type II groups are NO_2, CO_2Ak (Ak = alkyl), and $CONH_2$.

When a planar π-bonded group is attached to a π-bonded skeletal group at a position adjacent to another group, it is generally twisted through a dihedral angle, θ, due to repulsions between electrons in orbitals on non-bonded atoms. The steric effect exerted by an Xpπ group determines the dihedral angle θ. If the geometry of the system is known, it is then possible to calculate the effective van der Waals radius of Xpπ and therefore its effective v value.

In our earlier work in this field, we had no model of the geometry of this type of system and were therefore able to discuss steric effects of Xpπ groups only in terms of the extreme cases in which θ is 0° (Xpπ is coplanar with G) or 90° (Xpπ is perpendicular to G). In the former case the v value obtained is the largest that Xpπ can exert (Figure 1). Obviously, if $Z^1 \neq X^2$ there will be two v_{max} values, while if $Z^1 = Z^2$, there will be only one. Not only the steric parameter v but also the delocalized electrical effect parameter σ_D as well is a function of θ. When $\theta = 0$, π delocalization is at a maximum, and the σ_D value observed for the group should be the same as when the group is bonded to a position in G free of steric effects. An example is the para position in the benzene ring. When θ is 90°, the σ_D value should be 0 as π delocalization should not occur. It follows then that at intermediate values of θ, 0 < $\sigma_{D\theta}$ < $\sigma_{D,0}$, where $\sigma_{D\theta}$ is the value of σ_D for some value of θ between 0° and 90° and $\sigma_{D\theta}$ is the value of σ_D when θ is 0°.

Model of the Geometry. Consider an ortho-substituted benzene, **1**, bearing an Xpπ group, MZ^1Z^2, and a nonplanar substituent, Xnp. The proposed geometry of **1** (end view) is shown in Figure 3. We may define the group axis of
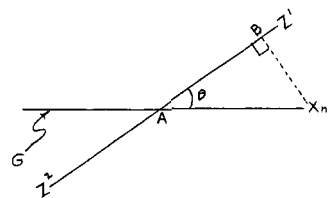
Figure 3. End view of 1, 2 - Xpπ(C_6H_4Xnp)Xpπ = MZ^1Z^2.
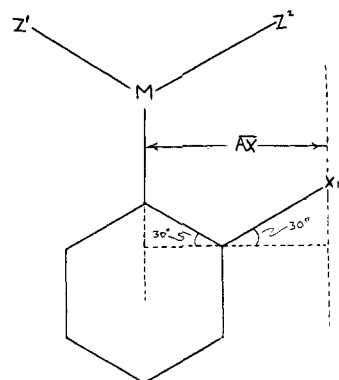
Figure 4. Top view of 1,2 - Xpπ(C_6H_4Xnp)Xpπ = MZ^1Z^2.

a substituent as a line collinear with the Xpπ-G bond. A is then the intersection of the Xpπ group axis with the line segment Z^1Z^2; B is the point on Z^1Z^2 at which the perpendicular to Z^1Z^2 through Xnp intersects. The distance $\overline{BX}$np is given by eq 2 in which $r_{V,min,Xp\pi}$ is the half-

$$BXnp = r_{V,Xnp} + r_{V,min,Xp\pi} = r + r' \quad (2)$$

thickness of Xpπ. From Figure 4 eq 3 is obtained, where

$$AX = l_{C,C} \cos 30° + l_{C,Xnp} \cos 30° \quad (3)$$

$l_{C,C}$ and $l_{C,X}$ are the bond lengths of the C–C and C–X bonds, respectively. The length of any bond may be written as the sum of the covalent radii, r_C, of the bonded atoms. Then

$$l_{C,Xnp} = r_{C,C} + r_{C,Xnp}; l_{C,C} = 2r_{C,C} \quad (4)$$

Thus

$$AX = (3r_{C,C} + r_{C,X}) \cos 30° \quad (5)$$

It is well-known that covalent radii are a linear function of van der Waals radii (eq 6). The from eq 5 and 6, as

$$r_{V,X} = r_{C,X} + b \quad (6)$$

$r_{C,C}$, the covalent radius of carbon, is constant

$$AX = (3r_{C,C} - b) \cos 30° + \cos 30° \, r_{VX} \quad (7)$$

$$= a_{11} \, r + a_{10} \quad (8)$$

The sine of θ may be written as in eq 9. Taking the

$$\sin \theta = \frac{BX}{AX} = \frac{r + r'}{a_{11}r + a_{10}} \quad (9)$$

reciprocal of eq 9 and then dividing through by $r + r'$ gives eq 10. As r' is constant within a data set because Xpπ

$$\frac{1}{\sin \theta} = a_{11} + \frac{(a_{10} - l_{11}r')}{r + r'} \quad (10)$$

is constant throughout the data set

$$\frac{1}{\sin \theta} = \frac{a_{30}}{r + r'} + a_{11} = \frac{a_{30}}{\sum r} + a_{11} \quad (11)$$

Results and Discussion

To provide a test of the validity of our model of the geometry, we have correlated data taken from the litera-

Table I. Dihedral Angles (in Degrees)

(1) 2-XC₆H₄Y, X-ray diffraction
   X, θ: F,^{a,b} 6.7; Cl,^{a,c} 13.7; Br,^{a,d} 18.3; SO₃⁻,^{a,e} 50.7;
   Cl,^{f} 7.1; Br,^{f} 13.1
(2) 2,2′-(XC₆H₄)₂, electron diffraction^g
   X, θ: Br, 75; F, 60; I, 79; Cl, 74; H, 42
(3) 2,2′-X¹C₆H₄-C₆H₄X², photoelectron spectroscopy^h
   X¹, X², θ: Cl, H, 66; OH, H, 68; Me, H, 70; Et, H, 70;
   NH₂, H, 71; I, H, 82; F, H, 49; H, H, 42; Me, Me, 78;
   Pr, H, 70; i-Pr, H, 70; Bu, H, 70; Br, Br, 75; F, F, 60
(6) 2,2′-(XC₆H₄)₂, dipole moment, PhH, 25 °C^i
   X, θ: F, 79; Cl, 82; Br, 85; I, 84
(7) 2-XC₆H₄CONH₂, dipole moments, dioxane^j
   X, θ: F, 32; Cl, 76; Br, 81; I, 71; H, 39
(8) 2-XC₆H₄CONH₂, molar Kerr constants, dioxane^j
   X, θ: F, 65; Cl, 79; Br, 76; I, 71
(9) 1-acetyl-2-alkylcyclohexenes, UV^k
   X, θ: Me, 31; Et, 36; Pr, 41; Bu, 48; Am, 49
(10) 2-AkC₆H₄NMe₂, UV^l
   X, θ: Me, 50; Et, 56; i-Pr, 58; t-Bu, 78
(11) 2-XC₆H₄NMe₂, UV^m
   X, θ: F, 33; Cl, 44; Br, 54; Me, 60
(12) (E)-PhXC=CXPh, UV, heptane^n
   X, θ: Me, 58; Et, 63; Cl, 39; Br, 54.5; I, 75.7
(13) 2-XC₆H₄Ac, ¹³C NMR^o
   X, θ: Me, 24; Et, 25; i-Pr, 29; t-Bu, 51; MeO, 17; Cl, 22;
   Br, 24; I, 29
(14) 2-X-4-F-C₆H₃Ac, ¹⁹F NMR^p
   X, θ: H,^{q} 33; F, 31; Cl, 42.5; Br, 45; I, 47; Me, 35;
   OEt, 31; OMe, 31
(15) 2-X-4-F-C₆H₃CH=CH₂, ¹⁹F NMR^p
   X, θ: H,^{q} 32; Cl, 33; Br, 36; I, 45; Me, 28
(16) 2,6-disubstituted 4-bromobiphenyls, ¹H NMR^r
   X, θ: H, 33; F, 49; Cl, 69; Br, 71; I, 78
(17) 2-O₂N-1,4-Ak₂C₆H₃, ¹H NMR^s
   X, θ: Me, 34; Et, 40; i-Pr, 47; t-Bu, 65

^{a} Y = CO₂H. ^{b} Ferguson, G.; Islam, K. M. S. *Acta Crystallogr.* **1966**, *21*, 1000. ^{c} Ferguson, G.; Sim, G. A. *Ibid.* **1961**, *14*, 1262. ^{d} Ferguson, G.; Sim, G. A. *Ibid.* **1962**, *15*, 346. ^{e} Okaya, Y. *Ibid.* **1967**, *22*, 104. ^{f} Y = C≡CH: Ferguson, G.; Tyrrell, J. *Chem. Commun.* **1965**, 195. Ferguson, G.; Islam, K. M. S. *J. Chem. Soc. B* **1966**, 593. ^{g} Bastiansen, O. *Acta Chem. Scand.* **1950**, *4*, 926. Bastiansen, O.; Smedvik, L. *Ibid.* **1954**, *8*, 1593. ^{h} Reference 5. ^{i} Minkin, V. I.; Osipov, O. A.; Zhdanov, Y. A. "Dipole Moments in Organic Chemistry"; Plenum Press: New York, 1970; p 150. ^{j} Pierens, R. K.; Williams, A. J. *J. Chem. Soc., Perkin Trans. 2* **1980**, 235. ^{k} Graves, J. K.; Jones, N. *Tetrahedron* **1969**, *25*, 223. ^{l} Burgers, J.; Hoefnagel, M. A.; Verkade, P. E.; Visser, H.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1958**, *77*, 491. ^{m} Klevens, H. B.; Platt, J. R. *J. Am. Chem. Soc.* **1949**, *71*, 1714. ^{n} Bruylants, A.; Leroy, G.; Van Meerssche, M. *Bull. Soc. Chim. Belg.* **1960**, *69*, 5. ^{o} Dhami, K. S.; Stothers, J. B. *Tetrahedron Lett.* **1964**, 631. ^{p} Belsham, M. G.; Muir, A. R.; Kinns, M.; Phillips, L.; Twanmoh, L. M. *J. Chem. Soc., Perkin Trans. 2* **1974**, 119. ^{q} Excluded from the correlation. ^{r} Reference 8. ^{s} Franck, R. W.; Williamson, M. A. *J. Org. Chem.* **1966**, *31*, 2420.

ture with eq 11 using linear regression analysis. The data used in the correlations are set forth in Table I, values of 100R² in Table III. The complete statistics for all correlations are presented in Tables I and II of the supplementary material (designated SM).

X-ray Diffraction Data. Values of θ are available for four 2-substituted benzoic acids with nonplanar substituents. This set (set 1) gave results significant at the 95% confidence level (CL), the equation accounting for 95% of the variance of the data. The van der Waals radii for monatomic groups used in the correlation are from Bondi.[4]

(1) Charton, M. *Prog. Phys. Org. Chem.* **1971**, *8*, 235. Charton, M. *J. Org. Chem.* **1975**, *40*, 407. Charton, M. In "Correlation Analysis in Chemistry: Recent Advances"; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; p 175.

Those for other groups are in this set, and the others described below are reported in Table II. The values for planar π-bonded groups are the half-thicknesses reported by Bondi.

We have also examined the possibility of including data for more than one type of Xpπ group in the same correlation. In set 1A are included the four 2-substituted benzoic acids of set 1· and two 2-substituted phenyl ethynyl ketones, 2-XC₆H₄COC≡CH. Although once again the correlation was significant at the 95% CL the equation accounted for only 75% of the variance of the data. Thus, although these results are not conclusive, it seems best to hold Xpπ constant within a given data set.

Electron Diffraction Data. Values of θ have been determined for four 2,2′-disubstituted biphenyls. The results show that in the preferred conformation the 2 and 2′ substituents should be in contact. We have therefore chosen to set ∑r in eq 11 equal to 2r_{V,Xnp}. Correlation with eq 11 gave significant results, accounting for 94% of the variance of the data.

Photoelectron Spectroscopy Data. Maier and Turner[5] reported a linear relationship between ΔE for substituted biphenyls and cos θ (eq 12), where I₄ and I₁

$$\Delta E = I_4 - I_1 \qquad (12)$$

and the fourth and first ionization potentials, respectively, of the biphenyl. Correlation of the θ values reported with eq 11 gave significant results (set 3A), accounting for 69.5% of the variance of the data. This set includes both 2-substituted and 2,2′-disubstituted biphenyls. As the correlation equation, although significant, fails to account for about 30% of the variance of the data, we correlated the θ values for 2-substituted and 2,2′-disubstituted biphenyls separately with eq 11 (sets 4A and 5A, respectively). Biphenyl itself is, of course, a member of each of these sets. Set 4A gave somewhat better results, accounting for 73% of the variance of the data while set 5A gave results accounting for 90%. Exclusion of the θ values for X = OH and NH₂ from set 4A gave very much improved results with the correlation equation, now accounting for 93% of the variance of the data. Further exclusion of the values for X = Pr, Bu, and i-Pr (set 4C) resulted in an improved correlation equation accounting for 96% of the variance of the data. Consideration of the θ values for the alkyl groups shows that they are all essentially the same. This is reasonable for X = Me, Et, Pr, and Bu if the steric effect is due only to the first C atom of the alkyl group. Then, using the r_V value for Et for the Me, Pr, and Bu groups and excluding X = OH, NH₂, and i-Pr from the 2-substituted biphenyls give set 4D for which excellent results are obtained.

Sets 4D and 5A have slopes and intercepts which are the same. Nevertheless, when they are combined into a single set (3B), only 87% of the variance of the data is accounted

(2) Aslam, M. H.; Burden, A. G.; Chapman, N. B.; Shorter, J.; Charton, M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 500. Aslam, M. H.; Chapman, N. B.; Shorter, J.; Charton, M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 720. (b) Charton, M.; Gawinecki, R.; Rasala, D.; Lenard, Z.; Tomasik, P. "Abstracts, EUCHEM Conference on Correlation Analysis in Organic Chemistry"; Assisi, Italy, 1979; pp 0–3.

(3) We have adopted as a system of nomenclature for correlation equations the coefficients of the substituent parameters in the equation. These are defined as L for σ_I, D for any of the σ_R constants, and S for steric parameters. Thus, the LD equation is one in which the substituent parameters are σ_I and one of the σ_R constants while the LS equation is a relationship in which the substituent parameters are σ_I and υ.

(4) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(5) Maier, J. P.; Turner, D. W. *Faraday Discuss. Chem. Soc.*, **1972**, *No. 54*, 149.

Table II. Values of r_V, σ_R^+, and σ_{50}

X	r_V	σ_R^{+g}	σ_{50}^h	X	r_V	σ_R^{+g}	σ_{50}^h
H	1.20[a]	0	0	Me	1.72[b]	−0.25	−0.17
Et	1.76[c]	−0.28	−0.15	Pr	1.88[c]	−0.31	
Bu	1.88[c]	−0.33		Am	1.88[c]	−0.33	
i-Pr	1.96[c]	−0.34		t-Bu	2.44[c]	−0.33	
F	1.47[a]	−0.39	0.06	Cl	1.75[a]	−0.41	0.22
Br	1.85[a]	−0.44	0.22	I	1.98[a]	−0.58	0.24
OMe	1.56[d]			OEt	1.68[d]		
OH	1.52[b]	−0.72		NH$_2$	1.55[b]	−1.05	
SO$_3^-$	2.19			NO$_2$	0.35[f,e]		
Ph	0.57[a,e]			XC$_6$H$_4$	0.57[a,e]		
Ac	0.50[a,e]			CONH$_2$	0.50[a,e]		
CH=CH$_2$	0.57[a,e,f]			CO$_2$H	0.50[a,e]		

[a] Reference 4. [b] Reference 1. [c] From v values reported in: Charton, M. *J. Am. Chem. Soc.* 1975, *97*, 1552 and the equation $r_{VX} = v_X + 1.20$. [d] From v values reported in Charton, M. *J. Org. Chem.* 1977, *42*, 3531 and the equation in footnote c. [e] Half-thickness. [f] Assumed equal to the value for Ph. [g] Charton, M., unpublished results.[6] [h] Reference 7.

Table III. Values of $100R^2$ [a]

set	$100R^2$	set	$100R^2$	set	$100R^2$	set	$100R^2$
1	95.18	4D	95.52	11A	99.17	17	90.40
1A	75.15	5A	90.09	12	21.25	51	92.25
2	93.16	6	38.71	12A	99.09	52	83.57
3A	69.51	7	59.66	13	92.01	55	93.73
3B	87.11	8	55.69	14	77.56	61	99.95
4A	72.99	9	90.30	14A	89.01	62	98.85
4B	93.24	10	92.40	15	92.89		
4C	95.58	11	74.48	16	94.33		

[a] $100R^2$ is the percent of the variance of the data accounted for by the correlation equation.

for by the correlation equation. If we correlate the data with eq 13, where n is the number of X groups bonded to

$$1/\sin\theta = \frac{b_{11}}{\sum r} + b_{12}n + b_{10} \qquad (13)$$

the biphenyl (set 51C), the results are improved, accounting for 92% of the variance of the data (Table I-(SM)). The coefficient b_{12} is significant although barely so.

We believe that this result can be accounted for as follows. We have shown elsewhere that ionization potentials of benzene derivatives can be correlated by the LD equation,[6] in the absence of steric effects. If steric effects are present, then the LDS equation can be used. Then

$$I_{4X} = L_4\sigma_{IX} + D_4\sigma_{DX} + S_4 v_X + h_4 \qquad (14)$$

and

$$I_{1X} = L_1\sigma + D_1\sigma_{DX} + S_1 v_X + h_1 \qquad (15)$$

From eq 12

$$\Delta E =$$
$$(L_4 - L_1)\sigma_{IX} + (D_4 - D_1)\sigma_{DX} + (S_4 - S_1)v_X + h_4 - h_1 \qquad (16)$$

The basis of the Maier and Turner method is that $L_4 = L_1$ and $D_4 = D_1$, while $S_4 \neq S_1$. We can account for the success of eq 13 and the deviation of OH and NH$_2$ if $D_4 - D_1$ is small but significantly different from 0. Of the X studied, σ_D is largest for OH and NH$_2$, and, furthermore, the σ_D term will be more important for disubstituted biphenyls than for the monosubstituted compounds.

To provide evidence for this argument, we have correlated all of the θ values in set 3 with eq 17. The results

$$1/\sin\theta = b_{11}/\sum r + D\sum\sigma_R^+ + b_{10} \qquad (17)$$

are given in Table II(SM) (set 52). They do indeed support the above discussion. The correlation equation accounts for 93.6% of the variance of the data, with D' being significant at the 98% confidence level. The σ_R^+ constants were specifically defined for use in the correlation of ionization potentials of substituted benzenes and benzene derivatives.[6] The values used here are given in Table II.

Dipole Moments and Molar Kerr Constants. Dihedral angles calculated from dipole moments have been reported for 2,2′-dihalobiphenyls (set 6). No significant correlation with eq 11 was obtained. With the exception of X = I, the θ values calculated from the dipole moment are very different from those obtained from photoelectron spectroscopy or electron diffraction. This difference may be due to the fact that the dipole moment results were determined in solution rather than in the gaseous state. Taken with the small size of the set (4 points), we believe the lack of correlation is not meaningful.

Values of θ for 2-substituted benzamides have been determined from dipole moments (set 7) and molar Kerr constants (set 8). Neither of these sets gave significant correlation with eq 11. Our results for the photoelectron spectral data suggested the possibility that θ might be a function of electrical effects as well as of $1/\sum r$. We have therefore examined the correlation of the dipole moment θ values with eq 18, in which the σ_{50} parameter is a com-

$$1/\sin\theta = b_{11}/\sum r + \rho\sigma_{50} + b_0 \qquad (18)$$

posite electrical-effect substituent constant. In the general case these constants, σ_T are defined by eq 19.[7] Any com-

$$\sigma_T = \sigma_I + (P_D/P_L)\sigma_D \qquad (19)$$

posite substituent constant is a combination of the localized electrical effect represented by σ_I and the delocalized electrical effect represented by σ_D. Then

(6) Charton, M.; Charton, B. I. "Abstracts, EUCHEM Conference on Correlation Analysis in Organic Chemistry"; Assisi, Italy, 1979; pp 0–1. Charton, M. "Abstracts of Papers", 2nd Chemical Congress of the North American Continent, Las Vegas, NV, 1980; American Chemical Society: Washington, DC, 1980; Abstract PHYS 244.

(7) Charton, M. *Prog. Phys. Org. Chem.* 1981, *13*, 119.

$$\sigma_T = \lambda\rho_I + \delta\sigma_D \qquad (20)$$

The percent delocalized and localized effects, P_D and P_L, respectively, are

$$P_D \equiv \frac{\delta 100}{\lambda + \delta} \qquad (21)$$

$$P_L = 100 - P_D \qquad (22)$$

The composite constants are designated σ_{P_D}, and thus σ_{50} constants are those for which P_D is 50. The constants used here are reported in Table II.

Correlation with eq 18 is marginally successful, the regression equation is significant at the 90% confidence level and accounts for 94% of the variance of the data (set 55, Table IISM). Unfortunately, as $1/\sum r$ and σ_{50} are highly correlated, no conclusion can be drawn from this set. No certain conclusion can be made with regard to whether dihedral angles determined from dipole moments fit the proposed geometric model until much more extensive data sets are available.

UV Spectra. Values of θ for 1-acetyl-2-alkylcyclohexanes gave a significant correlation with eq 11 (set 9). Dihedral angles of 2-alkyl-N,N-dimethylanilines also gave meaningful results (set 10). The dimethylamino groups is shallowly pyramidal rather than coplanar. Nevertheless, it may be treated as a quasi-planar π-bonded group. Significant correlation with eq 11 was not obtained for set 11 which includes both 2-halo- and 2-methyl-N,N-dimethylanilines. Exclusion of the value for X = Me did give a significant correlation (set 11A). The θ values for (E)-1′,2′-disubstituted stilbenes (set 12) also are not correlated by eq 11. If the two alkyl groups are excluded, significant correlation is obtained (set 12A). These results suggested the possibility that it might be necessary to take electrical effects into account. Sets 11 and 12 were therefore correlated with eq 18. For both sets, significant results were obtained (sets 61 and 62, respectively, Table II(SM)). Thus, as was observed above, for dihedral angles determined from photoelectron spectroscopy, both steric and electrical effects are important in determining θ.

NMR Spectra. Values of θ for 2-substituted acetophenones have been determined from ^{13}C chemical shifts, and they are well correlated by eq 11 (set 13). Values of θ for 2-substituted 4-fluoroacetophenones give a significant correlation on exclusion of the value for X = H (set 14). The results are improved if the r_V value for OMe is used for OEt (set 14A). This is reasonable if the steric effect is exerted by the OCH_2 fragment of the group and is analogous to the behavior of the propyl and butyl groups in the 2-alkylbiphenyls described above.

Dihedral angles for 2-substituted 4-fluorostyrenes have also been determined by ^{19}F NMR. Again, this set gives a significant correlation with eq 11 (set 15). Values of θ for 4-bromo-4′-Z-2,6-X_2-biphenyls have been determined by ^1H NMR spectroscopy in nematic liquid crystalline solution (set 16), and they too are correlated by eq 11. Finally, ^1H NMR spectra have been used to determine dihedral angles for 2-nitro-1,4-dialkylbenzenes. Good results were obtained on correlation with eq 11 (set 17).

Conclusions

Of the 15 sets studied, 13 gave significant correlations: nine with eq 11, and four with eq 17 or 18. The two sets of θ determined from dipole moments which do not fit eq 11 are short (four data points) and not well characterized (insufficient variation in substituent types). Two of the sets studied involve *cis*-vinylene skeletal groups; the remainder involve 2-phenylene (ortho) skeletal groups. The Xpπ groups in these sets include Ac, $CH{=}CH_2$, CO_2H, Ph, 2-X-C_6H_4, $CONH_2$, and NO_2. We may conclude then that the proposed model of the geometry does indeed account for the observed dihedral angles. The successful correlations with eq 17 and 18 further show that both electrical and steric effects may be important in determining the dihedral angle.

Field and Sternhell[8] have recently observed a smooth monatomic relationship between the dihedral angle and the van der Waals radius of Xnp. They did not propose an equation which related θ to r_{VX}, however, as we have done here. Our results are further supported by a previous study in which it was shown that for many simple molecules bond angles are a function of the van der Waals radii of the bonded groups.[9]

Overall, with the possible exception of the dipole moment data, the results support the proposed geometry. They lead to the following conclusions.

(1) The dihedral angle between a planar π-bonded skeletal group, Gpπ, and an Xpπ substituent vicinal (ortho, cis, etc.) to an Xnp group is dependent on the van der Waals radius of Xnp and that of Xpπ (generally the Xpπ half-thickness).

(2) In some cases electrical effects are also important. These conclusions apply to all Xpπ and probably to all Gpπ.

(8) Field, L. D.; Sternhell, S. *J. Am. Chem. Soc.* **1981**, *103*, 738.

(9) Charton, M. *J. Am. Chem. Soc.* **1979**, *101*, 7356.