Polarization of π-Electron Systems by Substituent Dipoles and Poles

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Theoretical calculations, at the *ab initio* STO-3G, 3-21G, and 4-31G bases, have been used to investigate the polarization of π-electron systems by substituent dipoles and poles. Isolated molecule calculations show a dependence on the third power of the distance for dipoles and the second power for poles and give an approximate measure of the polarizability of different molecules such as ethylene, acetylene, benzene, and formaldehyde. Polarization of conjugated dienes and trienes leads to charge alteration in accord with simple resonance ideas rather than affecting the π-system as a whole. The π-system in benzenes undergoes polarization partly as a whole and partly in accord with resonance concepts.

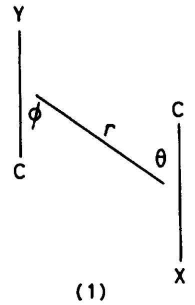
The polarization of π-systems by substituent dipoles has been the subject of numerous investigations[1-10] and some controversy. However, the polarization of an isolated multiple bond by a substituent at a relatively remote position is understood in broad detail. Thus, a considerable amount of experimental[1-4,6-10] and theoretical[2,5,8,9] evidence shows that the effect can be represented [see (1)] as the electrostatic polarization of a CY double or triple bond by a substituent (X) dipole. The magnitude of the effect can be understood in terms of equation (i), which refers[3] to the polarization energy along the CY bond arising from the substituent dipole (μ). (There is, however, still some[5] debate concerning the appropriate power of *r*.) For example, the directions of carbon-13 substituent chemical shifts in series such as $CH_2{=}CH{-}[CH_2]_nX$,[1] $N{\equiv}C{-}[CH_2]_2X$,[9] and 4-substituted bicyclo-octyl cyanides[6] are explicable in such terms and their magnitude is approximately proportional to the substituent field parameter (σ_F,[11,12] that is σ_I in earlier terminology) which is determined by the substituent dipole. Theoretical calculations of the polarization of ethylene[2,5] or formaldehyde[5] molecules by an isolated CH_3X molecule follow these principles.

$$\varepsilon = \mu\,(2\cos\theta\cos\varphi - \sin\theta\sin\varphi)/r^3 \qquad \text{(i)}$$

However, if the π-system involved is conjugated, the nature of the resulting polarization is not so clear. For the case of benzene it has been suggested that the system is polarized as a whole, but two alternative representations have been proposed as shown schematically in (2)[7] and (3).[8] Experimental evidence from carbon-13 substituent chemical shifts in 4-substituted bicyclo[2.2.2]octan-1-ylbenzenes (4) seems[3,4] to favour (2), whereas some similar shifts in ω-substituted alkyl benzenes (5) have been claimed[8] to favour (3). It has been suggested[4] that the null point in the π-electron polarization of benzene is dependent on the distance of the dipole from the π-system.

Investigations of the polarization of polyenes or related systems are more limited.[5,13] On the basis of theoretical calculations (STO-3G), it has been suggested[5] that the polarization of acrylaldehyde can be represented as partly resulting from local polarization of each double bond, as in (6a), and partly from extended polarization as in (6b).

In this paper, we report a systematic theoretical study of the nature and magnitude of the polarizations of π-electron systems. It has been shown earlier[2,5,12,14] that isolated molecule calculations provide an excellent basis for the study of the field effects of substituents; in particular, we have shown that the HX (or HNH_3^+) system is a satisfactory probe. Recent results[15] suggest that atomic electron populations obtained at the *ab initio* molecular level give a reasonable picture of the electron distribution in the molecule.



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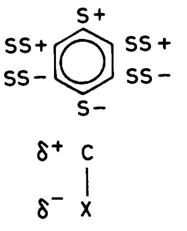

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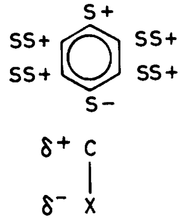

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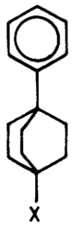

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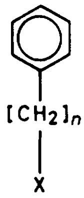

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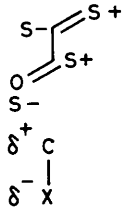
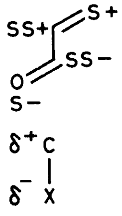


(6a)

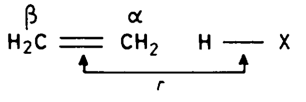


(6b)

Table 1. Polarization (3-21G) of the π-system of ethylene by HF and by NH_4^+ (Δq_π in 10^4 electrons, r [a] in Å, atomic populations increase at C_α, decrease at C_β)

HF		NH_4^+	
r	Δq_π	r	Δq_π
4	258	4	1 270
5	139	6	552
6	82	8	310
7	52	10	199
8	35	12	138
10	18		

[a] Distance from centre of C=C bond to centre of HF bond in HF or to nitrogen atom in NH_4^+.



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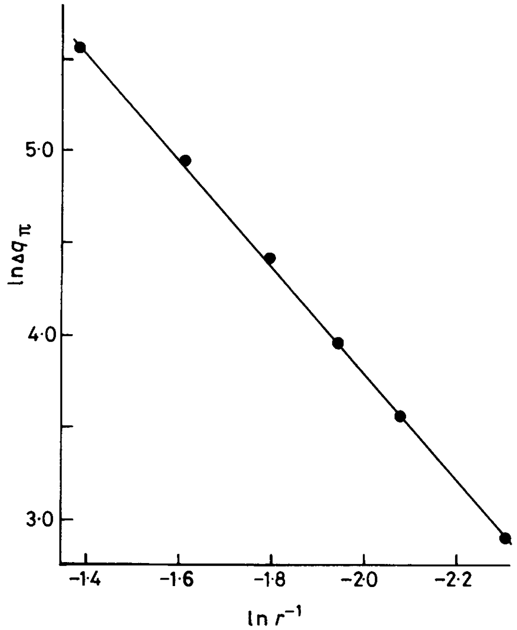


Figure 1. Plot of ln Δq_π *versus* ln r^{-1} for the polarization of ethylene by HF

We have therefore looked at the polarization of molecules such as ethylene, acetylene, benzene, butadiene, hextriene, and styrene by substituent dipoles and poles at various geometries.

All calculations were performed at the *ab initio* STO-3G, 3-21G, or 4-31G level, using the Gaussian-80 program [16] and standard molecular geometries.[17]

Results and Discussion

The results are given in Tables 1—8. The atomic electron populations are shown as differences from appropriate standards expressed in 10^4 electrons.

Table 1 shows the polarization of the π-electron system of ethylene by HF, or alternatively by NH_4^+, at various distances. The geometry is as shown in (7), the Table showing the increase in π-electron population at C_α, which is necessarily balanced by a similar decrease at C_β.

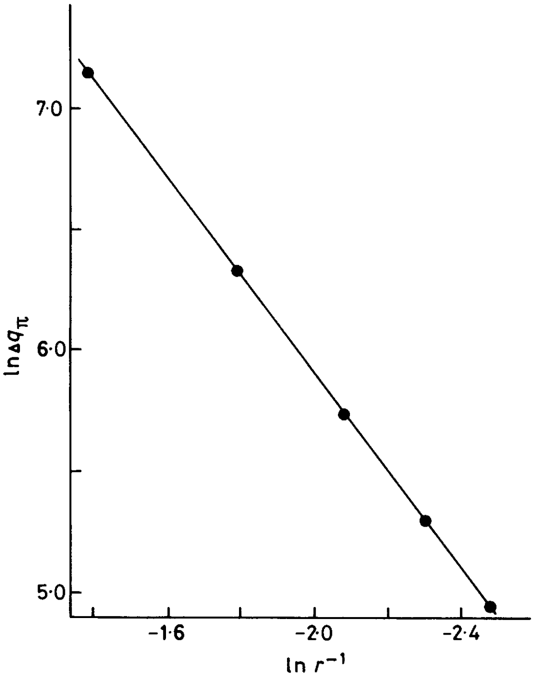
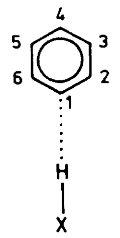
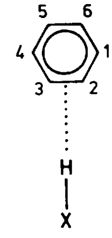


Figure 2. Plot of ln Δq_π *versus* ln r^{-1} for the polarization of ethylene by NH_4^+



(8a)



(8b)

The first point of interest is that the polarization by HF approximately follows $1/r^3$, as expected from equation (i). This is shown in Figure 1 which gives a plot of ln Δq_π versus ln r^{-1}. The fit is excellent and the slope shows the polarization to be dependent on $r^{2.90}$. There has been some dispute as to the power of r involved but clearly it is approximately 3; a value of 2.85 was found [5] for the polarization of formaldehyde by methyl fluoride. The value does also depend on the way in which r is defined. Figure 2 shows the corresponding plot for the polarization of the π-system of ethylene by the charged ammonium group when r is taken as the distance from the mid-point of the π-system to the nitrogen atom. Once again an excellent fit is obtained and the slope gives a polarization proportional to $1/r^{2.01}$. The dependence on $1/r^2$ is in accord with the one lower power of distance dependence of coulombic effects on poles as compared with dipoles.

Table 2 shows the corresponding polarizations of the π-system of benzene by HF and by NH_4^+ in both configurations (8a) and (8b) at various distances. For (8a), a similar analysis to that used with ethylene shows an approximate fit with $1/r^3$ (HF) or $1/r^2$ (NH_4^+), provided that r is taken from the centre of the HF bond to C(1) rather than to the centre of the benzene ring. This suggests that the primary polarization is

Table 2. Polarization (STO-3G) of the π-system of benzene by HF and by NH_4^+ [A, along C(1),C(4) axis; B, along axis bisecting C(2),C(3) and C(5),C(6); Δq_π in 10^4 electrons, −ve indicates increase over 1.000 electrons; *r* in Å)

A, HF

r[a]	C(1)	Δq_π C(2)[C(6)]	Δq_π C(3)[C(5)]	C(4)
2	−100	19	11	40
3	−47	5	9	20
4	−26	1	6	12
5	−16	−1	4	8
6	−10	−1	3	5

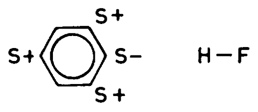
A, NH_4^+

r[b]	C(1)	Δq_π C(2)[C(6)]	Δq_π C(3)[C(5)]	C(4)
3	−526	−12	139	271
5	−220	−37	81	133
7	−125	−31	51	83
9	−80	−24	35	57
12	−48	−16	22	37

B, *r* = 4 Å[c]

	C(2)[C(3)]	C(1)[C(4)]	C(5)[C(6)]
Δq_π HF	−29	12	16
Δq_π NH_4^+	−235	69	166

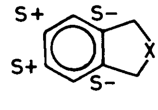
[a] Distance from H attached to C(1) to H of HF. [b] Distance from H attached to C(1) to N of NH_4^+. [c] Distance from centre of C(2),C(3) axis to H of HF or HNH_3^+.



(9)

at C(1), with the total π-system responding. The results also show that the null point shifts as HF moves further away; form (3) represents the polarization at close distances and (2) at longer range. This is in accord with earlier suggestions[4] based on experimental data. A similar trend is found in the polarization of the benzene π-system by NH_4^+, but here the electron population change is always in accord with (2) for the geometries employed. The polarization approximately follows $1/r^2$ where *r* is taken from the nitrogen to C(1).

A further examination of the polarization of the π-system of benzene by HF at close distances suggests a significant component as shown in (9). Thus, the π-electron population decreases more at C(2)[C(6)] than at C(3)[C(5)]. This is in accord with simple ideas of canonical structures assuming a prime polarization at C(1), leading to consequent depletion of population mainly at the *ortho-* and *para*-positions. The overall polarization therefore seems to be partly of the π-system as a whole and partly an uneven response to a prime polarization at C(1).



(X = O, S, NH *etc.*)

(10)

Table 3. Polarization (4-31G) of the π-system of ethylene by molecules HX (Δq_π in 10^4 electrons,[a] −ve indicates increase in π-population at C_α

X	*r* 4 Å[b]	4 Å[c]	5 Å[b]	7 Å[b]
F	−151	−122	−91	−40
OH	−95	−75	−57	−25
CN	−141	−120	−89	−41
NH_2	−45	−37	−27	−11
Me		2		
OMe		−75		
CF_3		−106		
CHO		−56		
COMe		−47		
NO_2		−171		

[a] Corrected for small effects where X = H (−8 at 4 Å, −4 at 5 Å, −2 at 7 Å). [b] Distance between C_α and H of HX. [c] Distance between C_α and H of HX bond (that is, C_α to *H*X distance is fixed in this series). Values calculated at 3—21 G basis.

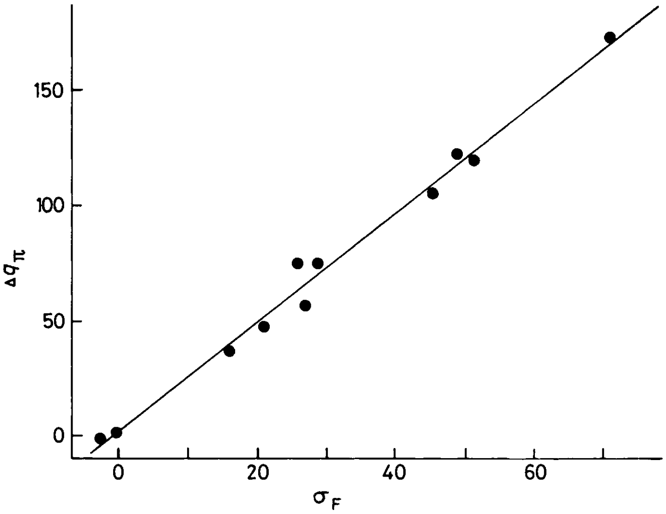


Figure 3. Plot of Δq_π for the polarization of ethylene by molecules HX *versus* σ_F values for X

For situation (8b), the polarization leads to an increase in electron population at C(2), C(3) and a decrease at C(5), C(6), with a lesser decrease at C(1), C(4). Earlier workers[18] had suggested a polarization mainly at C(2), C(3), and C(5), C(6) based on carbon-13 chemical shifts in compounds of type (10).

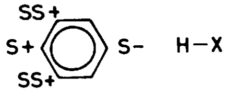
The size of the effect found here for C(1),C(6), particularly with HF, once again suggests that primary polarization at C(1) or C(6) may lead to considerable effects at other *ortho*-positions, in accord with simple resonance ideas.

Table 3 shows the polarization of the π-system of ethylene by various molecules HX [geometry as in (7)]. The first point of interest is that as X changes the polarization follows the corresponding σ_F value[12] as shown in Figure 3. This is in accord with earlier work[5,12,14,19] on the polarization of σ- and π-bonds. The relationship is clearly better than that found between the carbon-13 substituent chemical shift and σ_F for the sp^2 carbons of compounds $CH_2{=}CH{-}[CH_2]_nX$, where

Table 4. Polarization (STO-3G) of the π-system of benzene by molecules HX (Δq_π in 10^4 electrons, −ve indicates increase in π-population over 1.000 electrons; *r* taken to be equivalent to that in (4-substituted bicyclo-octyl)benzene

X	C(1)	C(2)[C(6)]	C(3)[C(5)]	C(4)
H	−5	1	0	2
NH_2	−11	1	2	5
OMe	−31	2[a]	7[a]	14
F	−42	4	8	19
Me	−3	1	0	1
CN	−52	2	2	24
CHO	−21	1[a]	5[a]	10
NO_2	−73	3	16	34
CO_2Me	−40	0[a]	11[a]	20
CF_3	−33	1	7	15

[a] Average with respect to conformation of HX.



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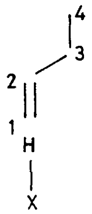
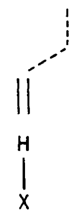


(12a)



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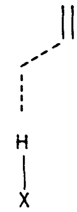


(12c)

other factors, such as conformational flexibility, can cause problems.[1]

A second interesting point is that whereas at shorter distances HF causes a greater polarization than HCN, the order is reversed for distances where *r* is greater than 5 Å. This illustrates the breakdown [1] of the point-dipole approximation at short distances. It is thus clear that a universal scale of exact σ_F values is not possible, as distance (and also angle for non-symmetrical substituents [20]) can cause relative changes between substituents.

Table 4 shows the polarization of the π-system of benzene by HX at a distance equivalent to that found in the corresponding 1-phenyl 4-substituted bicyclo-octanes (4). This allows comparison of our results with the carbon-13 substituent chemical shifts reported [3,4] for (4). The biggest changes are found at C(1) and C(4) in the benzene ring, with very small effects at C(2)[C(6)]. The changes in π-populations at C(1) and C(4) broadly follow σ_F. The polarization can be represented as in (11).

The carbon-13 substituent chemical shifts are similar, except that small upfield shifts (increase in population) are found at C(2)[C(6)].

Table 5 shows the polarization of the π-system of butadiene by HF and by NH_4^+. The figures for Δq_π are the differences between the values for butadiene and fo^{r} the butadiene–HF or butadiene–NH_4^+ systems (12a). Also shown are the Δq_π values corrected for the separate polarization of ethylene molecules at distances corresponding to both the unsaturated linkages in butadiene [(12b), (12c)].

Table 5. Polarization (STO-3G and 3-21G) of the π-system of butadiene by HF and NH_4^+ (calculated Δq_π values in 10^4 electrons with respect to butadiene,[a] −ve indicates increase in electron population; corrected values obtained after allowance for polarization of isolated ethylene molecules at corresponding distances for both double bonds)

STO-3G, HF

r[b]	2.5 Å		3.5 Å		4.5 Å	
	Calc.	Corr.	Calc.	Corr.	Calc.	Corr.
C(1)	−194	−37	−93	−17	−54	−12
C(2)	153	−4	73	−3	42	0
C(3)	−50	−16	−27	−5	−17	−2
C(4)	90	56	47	25	28	13

STO-3G, NH_4^+

r[b]	6 Å		10 Å	
	Calc.	Corr.	Calc.	Corr.
C(1)	−403	−95	−162	−42
C(2)	304	−4	120	0
C(3)	−188	−15	−86	−4
C(4)	287	113	127	45

3-21G

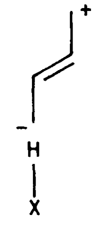
	HF, 3 Å[b]		NH_4^+, 6 Å[b]	
	Calc.	Corr.	Calc.	Corr.
C(1)	−285	−49	−425	−88
C(2)	223	−13	320	−17
C(3)	−86	−20	−214	−10
C(4)	147	81	319	115

[a] For butadiene, π-populations are 1.0089 at C(1), 0.9911 at C(2) at STO-3G basis, and 1.0187 at C(1), 0.9813 at C(2) at 3-21G basis. [b] Distance from C(1) of butadiene to H of HF or HNH_3^+.

Table 6. Polarization (STO-3G) of the π-system of hexatriene by HF (calculated Δq_π values in 10^4 electrons with respect to hexatriene,[a] −ve indicates increase in electron population; corrected values obtained after allowance for polarization of isolated ethylene molecules at corresponding distances for each double bond)

r[b]	2.5 Å		3.5 Å		4.5 Å	
	Calc.	Corr.	Calc.	Corr.	Calc.	Corr.
C(1)	−207	−50	−98	−22	−55	−13
C(2)	157	0	74	−2	41	−1
C(3)	−70	−36	−39	−17	−25	−10
C(4)	92	58	49	27	30	15
C(5)	−28	−17	−17	−8	−12	−6
C(6)	59	47	34	26	23	17

[a] In hexatriene, π-populations are C(1), 1.0108; C(2), 0.9905; C(3), 0.9988 at STO-3G basis. [b] Distance between C(1) and H of HF.



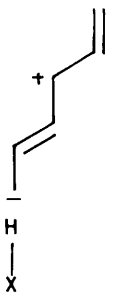
(13)

Thus, Δq_π (corr.) values show the additional effect found over that for isolated double bonds at corresponding distances. The Table shows that most of the additional effect occurs at atoms 1 and 4 in accord with a contribution from canonical form (13). There is also some evidence that part of the addition

Table 7. Polarization (STO-3G) of the π-system of styrene by HF (calculated Δq_π values in 10^4 electrons, with respect to styrene,[a] −ve indicates increase in electron population; corrected values obtained after allowance for polarization of isolated ethylene and benzene molecules at distances from HF corresponding to those in styrene)

r[b]	2.5 Å		3.5 Å		4.5 Å	
	Calc.	Corr.	Calc.	Corr.	Calc.	Corr.
C(1)	−203	−46	−98	−22	−56	−14
C(2)	158	1	76	0	44	2
C(3)	−59	−38	−26	−14	−14	−7
C(4)[c]	17	35	3	17	−1	9
C(5)[c]	7	−3	3	−3	1	−2
C(6)	43	32	21	13	12	6
C(7)[c]	6	−5	4	−4	4	−2
C(8)[c]	31	25	16	12	10	7

[a] In styrene, π-populations at STO-3G level are: C(1), 1.0047; C(2), 0.9952; C(3), 0.9912; C(4), 1.0055; C(5), 0.9966; C(6), 1.0038; C(7), 0.9966; C(8) 1.0064. [b] Distance between C(1) and H of HF. [c] C(4), C(5) are *cis* to double bond, C(7), C(8) are *trans*.



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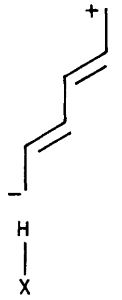

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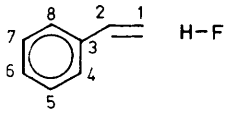
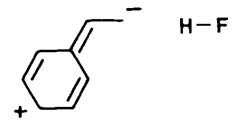


(15)

effect arises from an indirect polarization of the C(3)C(4) π-bond resulting from the polarization of the C(1)C(2) bond. There is little evidence for a polarization of the π-system as a whole. In particular, the value of Δq_π (corr.) at C(2) is very low. A similar result is found at the 3-21G level.

The polarization of the π-system of hexatriene (Table 6) gives additional evidence for the importance of resonance charge transfer. The ' Δq_π (corr.) ' figures again show the importance of forms such as (14a) and (14b) and that the polarization of the C(1)C(2) bond increases the polarization of the C(3)C(4) and C(5)C(6) bonds. Again, there is very little change at C(2), clearly indicating that overall polarization of the π-system as a whole is not important. These conclusions differ from those [5] given for polarization of acrylaldehyde, but those figures were limited and open to various interpretations.

We also examined the polarization of the π-system of styrene (Table 7), in view of the interest in this system.[2,21] The geometry used is shown in (15). The Δq_π figures, based on styrene as a standard, were corrected for the polarization of isolated ethylene and benzene molecules at the same geometry with respect to the HF molecule. These Δq_π(corr.) figures again show the importance of contributions from resonance forms such as (16) and corresponding ones involving carbons 4 and 8.



(16)

Table 8. Polarization (STO-3G and 3-21G) of the π-systems of various molecules by HF and NH_4^+ (calculated Δq_π values in 10^4 electrons with respect to unperturbed parent molecule, −ve shows increase in π-electron population)

		Δq_π			
		HF (4 Å)[a]		NH_4^+ (6 Å)[b]	
Molecule	Atom	3-G	3-21G	3-G	3-21G
Ethylene	C(1)	−74	−170	−308	−446
Butadiene	C(1)	−86	−202	−400	−563
Benzene	C(1)	−69	−166	−226	−322
Acetylene	C(1)	−41	−108	−170	−284
Formaldehyde	C	−54	−90	−197	−248
HCN	C	−31	−73	−125	−191

[a] Distance from C(1) or C to centre of HF bond. [b] Distance from C(1) to C or N atom.

The Δq_π corr figures are small for C(2), C(5), and C(7), indicating that polarization of the π-system as a whole is not important. The polarization of the ethylenic π-bond seems to lead to additional polarization at C(3), but this is mainly compensated for by decreases in π-electron populations at the *ortho*- and *para*-positions.

Relative Polarization of Different π-Systems.—It is also possible to compare approximately the response of different π-systems to a dipole. Thus in Table 8, the first heavy atom of each molecule was at a fixed distance from either HF (4 Å from centre of HF bond) or NH_4^+ (6 Å from N atom). The Δq_π value at the first heavy atom provides a rough measure of the polarization and the following order is obtained at the STO-3G or 3-21G basis sets:

$$\text{butadiene} > \text{ethylene} \geqslant \text{benzene} > \text{acetylene} > \text{formaldehyde} > \text{HCN}$$

Thus, the π-systems of triple bonds seem less polarizable than those of double bonds. This work is being extended to overall polarization including single bonds, and it is hoped to provide a theoretical scale of polarizability.

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References

1 E. A. Hill and H. E. Guenther, *Org. Magn. Reson.*, 1981, **16**, 177, and references therein.
2 W. F. Reynolds, P. G. Mezey, and G. K. Hamer, *Can. J. Chem.*, 1977, **55**, 522 and references therein.
3 W. Adcock and T. C. Khor, *J. Am. Chem. Soc.*, 1978, **100**, 7799.
4 D. Ewing and K. J. Toyne, *J. Chem. Soc., Perkin Trans. 2*, 1979, 243.
5 R. T. C. Brownlee and D. J. Craik, *J. Chem. Soc., Perkin Trans. 2*, 1981, 760.

6 G. Butt, N. Pirzada, R. D. Topsom, W. Adcock, and A. N. Abeywickrema, *Tetrahedron Lett.*, 1982, **23**, 2161.
7 R. T. C. Brownlee, G. Butt, M. P. Chan, and R. D. Topsom, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1486.
8 W. F. Reynolds, I. R. Peat, M. H. Freedman, and J. R. Lyerla, *Can. J. Chem.*, 1973, **51**, 1857.
9 G. Butt, J. Cilmi, P. M. Hoobin, and R. D. Topsom, *Spectrochim. Acta*, 1980, **36A**, 521.
10 J. Bromilow, R. T. C. Brownlee, D. J. Craik, P. F. Fiske, J. E. Rowe, and M. Sadek, *J. Chem. Soc., Perkin Trans. 2*, 1981, 753.
11 W. R. Reynolds, *Prog. Phys. Org. Chem.*, 1981, **13**, 1.
12 S. Marriott and R. D. Topsom, *Tetrahedron Lett.*, 1982, **23**, 1485.
13 See, for example: O. Kajimoto, and T. Fueno, *Tetrahedron Lett.*, 1972, 3329.
14 R. D. Topsom, *J. Am. Chem. Soc.*, 1980, **103**, 39.
15 S. Marriott and R. D. Topsom, *J. Mol. Struct.*, 1982, **89**, 83.
16 J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn, and J. A. Pople, 'Gaussian 80—An *Ab Initio* Molecular Orbital Program,' Department of Chemistry, Carnegie-Mellon University, Pittsburg, 1980.
17 J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.
18 W. Adcock, B. D. Gupta, and W. Kitching, *J. Org. Chem.*, 1976, **41**, 1498.
19 M. Taagepeera, W. J. Hehre, R. D. Topsom, and R. W. Taft, *J. Am. Chem. Soc.*, 1976, **98**, 7438; W. J. Hehre, M. Taagepeera, R. W. Taft, and R. D. Topsom, *ibid.*, 1981, **103**, 1344.
20 R. D. Topsom, *Prog. Phys. Org. Chem.*, 1976, **12**, 1.
21 G. K. Hamer, I. R. Peat, and W. F. Reynolds, *Can. J. Chem.*, 1973, **51**, 897, 915.

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