π-Electron Transfer as Calculated at Various Levels of Basis Set. A Redefinition of the Theoretical Scale of $\sigma_R°$ Values

Stephen Marriott, Anthony Silvestro, and Ronald D. Topsom *
Department of Chemistry, La Trobe University, Bundoora, Victoria, Australia 3083

Ab initio molecular orbital calculations are reported for the π-electron transfer to or from the substituent for 20 monosubstituted benzenes, both at the minimal STO-3G basis set and at the split-valence 4-31G basis set. Evidence from i.r. intensities, experimental $\sigma_R°$ values, rotational barriers, dipole moments, the protonation of cyanides XCN, and stabilisation energies all indicate that it is the STO-3G basis that better reproduces the experimental data for systems where π-electron transfer is important. The theoretical $\sigma_R°$ scale is redefined using π-electron transfers for monosubstituted ethylenes at the STO-3G//STO-3G basis.

It is generally expected that *ab initio* molecule orbital calculations give better agreement with experimental data as the basis set is increased from the minimal STO-3G to split-valence bases 3-21G and 4-31G. This certainly seems to be true[1] for calculations of molecular geometry and of properties such as electron distributions, dipole moments, and equilibrium energies for simple non-conjugated molecules. Occasional better agreement with experiment using the minimal basis set probably reflects an accidental cancellation of errors.[2]

Much less evidence has been presented to date concerning similar comparisons in molecules such as substituted acetylenes, ethylenes, and benzenes, where considerable π-electron transfer may be involved. In earlier work to establish a scale of theoretical $\sigma_R°$ parameters we found[3] that in such molecules calculations of the π-electron transfer at the split-valence basis gave a bilinear relationship against values at the minimal basis. Here the plot for π-electron-donating substituents had a different slope to that for π-electron-withdrawing groups. At that time, we used the higher level 4-31G results to determine[4] the $\sigma_R°$ scale, assuming that it should be superior to the STO-3G basis set. Nevertheless, the theoretical $\sigma_R°$ values suggested a greater than expected π-electron withdrawal by groups such as NO_2 and NO.

Our recent studies on the effect of various levels of basis set in reproducing experimental data now lead us to reinvestigate this. Thus, we have found that rotational barriers[5] and dipole moments[6] of monosubstituted benzenes containing π-electron-withdrawing substituents, are better reproduced with the STO-3G basis set than with split-valence levels, but this is not true if π-electron donors are involved. Again, calculations[7] for the proton exchange equilibria (1) give closer agreement with

$$XCNH^+ + HCN \rightleftharpoons XCN + HCNH^+ \qquad (1)$$

experiment as the basis set is increased where X is alkyl or a π-electron donor, but the minimal basis set STO-3G results were superior when X was a π-electron-withdrawing group.

The aim of the present work was first to extend the calculations on monosubstituted benzenes, since many experimental data are based on these compounds. We have thus considerably extended the number of split-valence level calculations here. Further, we wished to investigate† whether STO-3G or 4-31G level calculations would better reproduce the energies of process (2), for substituents X where experimental data are available from heats of formation. On the basis of these results, plus a careful examination of the other data discussed above, we have redefined theoretical $\sigma_R°$ values using calculations on monosubstituted ethylenes at the STO-3G//STO-3G basis set. Calculations and observed $\sigma_R°$ values are reported for a considerable number of substituents.

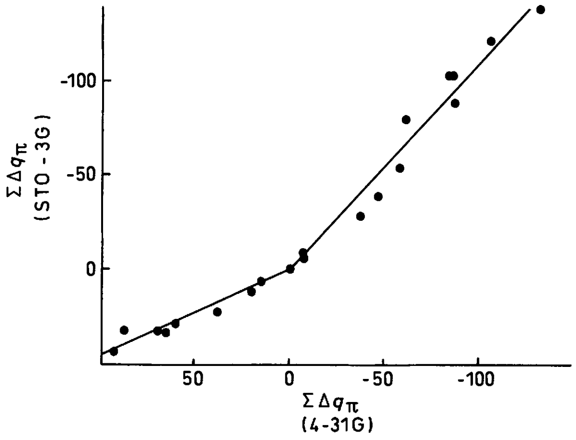
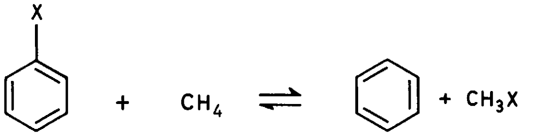


Figure 1. Plot of $\Sigma\Delta q_\pi$ for monosubstituted benzenes calculated at the STO-3G basis *versus* values calculated at the 4-31G basis



(2)

Calculations

All calculations were made at the *ab initio* molecular orbital STO-3G, 3-21G, or 4-31G levels, with the GAUSSIAN-82 program[8] with standard geometries[9,10] or optimization as indicated. The optimisation of substituted ethylenes and benzenes refers to all the bonds and angles in the substituent; the geometry of the vinyl or phenyl group was kept constant. Electron transfers were determined by a Mulliken population analysis.[11]

Results and Discussion

In Table 1 we list the calculated π-electron transfer to (+ sign) or from (− sign) the substituent for a variety of monosubstituted benzenes.‡ Figure 1 shows a plot of these results as calculated at the 4-31G basis *versus* those at the STO-3G basis set. The

---

† We thank Professor J. A. Pople for suggesting this idea.

‡ The energies are available on request from the authors.

Table 1. Calculated total π-electron transfer ($\Sigma\Delta q_\pi$) for monosubstituted benzenes, C_6H_5X (values in 10^3 e)

	$\Sigma\Delta q_\pi$		
X	STO-3G	4-31G	$A^{\frac{1}{2}a}$
$NMe_{2(pl)}$	−137	−134	70.7
$NH_{2(pl)}$	−120	−109	62.0
$NH_{2(tetr)}$	−88	−88	
OMe	−102	−85	56.8
OH	−102	−86	53.3
SMe	−53	−59	33.1
SH	−38	−48	25.8
F	−71	−57	45.3
Cl	−28	−38	28.8
Me	−8	−9	13.2
CH_2F	−7	−9	
H	0	0	0
$CHCH_2$	0	4	6.6
CCH	6	15	9.5
CF_3	11	20	14.7
CN	22	38	11.3
CHO	32	70	32.4
COMe	28	61	29.0
CO_2Me	33	66	20.6
NO_2	31	88	23.1
NO	43	93	9.4

[a] Ref. 15.

Table 2. Calculated and experimental energies for process (2) — see text (values in kJ mol^{-1})

	STO-3G	STO-3G// STO-3G	3-21G	3-21G// 3-21G	Experiment
Phenol	51.9	56.4	49.7	50.6	52.1
$Benzaldehyde_{(pl)}$	28.3	32.4	39.3	40.3	28.6

plot is clearly bilinear with results for π-electron-withdrawing substituents being on a different line to π-electron donors as suggested earlier[3] with a more restricted number of substituents. The slope is 0.93 for the π-electron donors and 2.25 for the π-electron withdrawers, showing the very marked difference. Quite apart from the interest in the performance of various levels of basis set, it is important to investigate this thoroughly because of the use of such data in determining[4] resonance parameters ($\sigma_R°$), which in turn are used[12] to analyse experimental data. The $\sigma_R°$ parameters are a measure of the ability of a substituent to donate or withdraw π-electrons from an attached system. A reliable theoretical scale should give values free from the effect of solvent or other intermolecular interaction.

Recently, evidence has accumulated which suggests that the problem is that calculations at the split-valence overestimate the π-electron transfer and related energy of resonance-withdrawing groups such as CHO, NO_2, and NO. Thus, the calculated[5] two-fold barrier to rotation in phenol is 21.6 kJ mol^{-1} at the STO-3G level, 17.6 at STO-3G//STO-3G, 10.2 at 3-21G, 8.1 at 3-21G//3-21G, and 10.7 at 4-31G, compared with an experimental value of *ca.* 14 kJ mol^{-1}. However, for benzaldehyde, the corresponding calculated values are 27.6, 24.3, 48.1, 46.7, and 40.7 kJ mol^{-1}, compared with an experimental value of 19.3 kJ mol^{-1} and split-valence level results are correspondingly too high by a factor of 2—3 for nitrobenzene, nitrosobenzene, and benzoyl fluoride. These findings are carried into calculations[6] of the dipole moments of monosubstituted benzenes. Here, much of the dipole arises from the electron distribution in the σ-electron system, but nevertheless, calculated dipole moments for molecules such as benzonitrile, benzaldehyde, and nitrosobenzene are too high at the split-valence and even at the 6-31G*//6-31G* basis, whilst agreement with experiment for molecules such as aniline and phenol is excellent. A similar result was found[7] for process (1). Here, results for X = NMe_2, halogen, or alkyl showed closer agreement with experiment as the basis set improved and were excellent at the 6-31G*//6-31G* level. Results where X was an π-electron-withdrawing substituent, by contrast, showed best agreement with experiment at the minimal basis level, and the disagreement at higher levels reflected a much greater than experimentally found effect. All these results thus suggest that the split-level and polarisation bases give good results for such conjugated systems where a π-electron-donating substituent is attached, but overestimate effects for π-electron-withdrawing groups. The bilinearity found in Figure 1 thus seems likely to arise from the same cause.

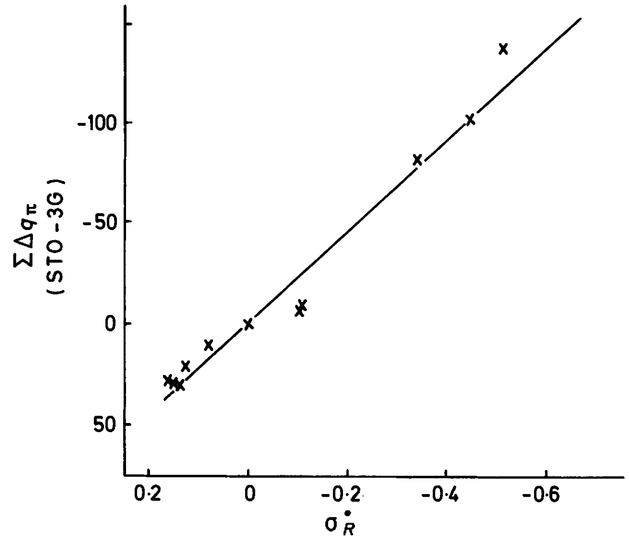


Figure 2. Plot of $\Sigma\Delta q_\pi$ for monosubstituted benzenes calculated at the STO-3G basis *versus* experimental $\sigma_R°$ values

As an additional check, we have calculated[8] (Table 2) the energies for process (2) at various levels of basis set. Reliable values for ΔH_f (gas) are somewhat limited for C_6H_5X and CH_3X, but we calculated ΔH_f values for phenol (52.1 kJ mol^{-1}) and benzaldehyde (28.6 kJ mol^{-1}) from values[13] of ΔH_f for the appropriate molecules involved in process (2). The calculated results for phenol show that the minimal STO-3G basis gives reasonable results, whilst split-valence levels give even better agreement with experiment. However, values for planar benzaldehyde are considerably overestimated in the positive direction at the split-valence level, whilst again being reasonable at the minimal basis. Once again, this fits in with an overestimate of the important of π-electron interaction for the CHO substituent when calculated at the split-valence level.

We conclude that there is a significant body of evidence to suggest that the minimal basis set is the appropriate one to use in such conjugated systems if it is desired to estimate experimental data. We now give further evidence for this by comparison of the calculated π-electron densities for monosubstituted benzenes with various experimental quantities.

The calculated values of the total π-electron transfer ($\Sigma\Delta q_\pi$) are plotted against values of $\sigma_R°$ obtained[14] by an analysis of reactivity and n.m.r. data, in Figures 2 (STO-3G) and 3 (4-31G). A satisfactory linear plot is obtained overall for the minimal basis calculations, but most of the π-electron-withdrawing groups are calculated at 4-31G to have a significantly bigger than expected value of $\Sigma\Delta q_\pi$. A similar result is found if the plots are made against the recently[12] determined $\sigma_R°$ values.

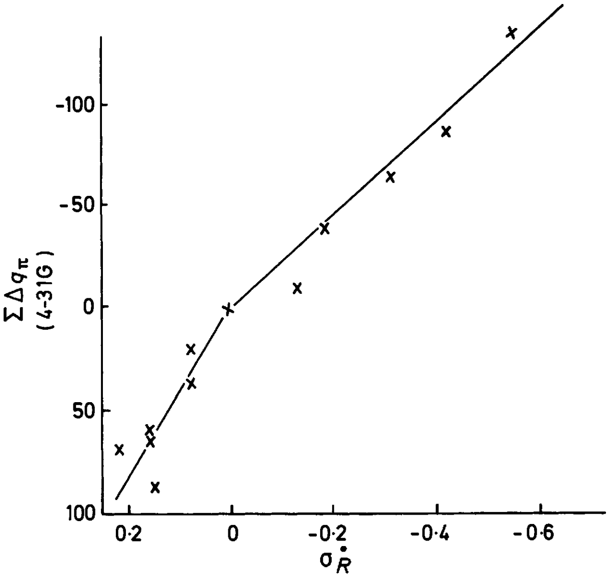


Figure 3. Plot of $\Sigma\Delta q_\pi$ for monosubstituted benzenes calculated at the 4-31G basis *versus* experimental $\sigma_R{}^\circ$ values

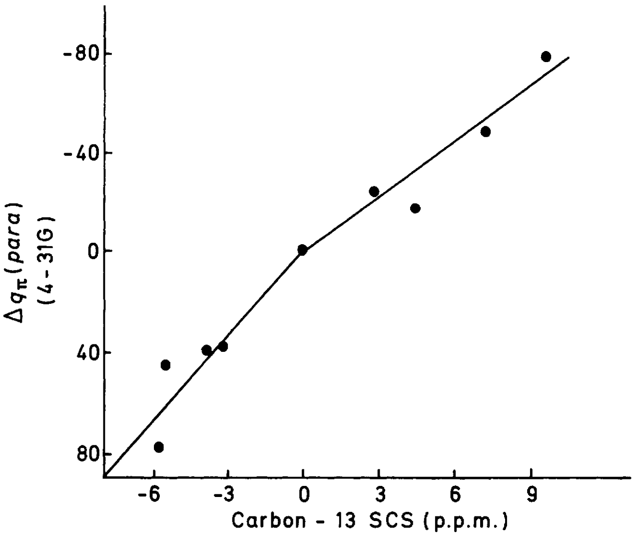


Figure 4. Plot of $\Delta q_{\pi(para)}$ for monosubstituted benzenes calculated at the 4-31G basis *versus* carbon-13 SCS for the *para*-carbon atom

We showed[14] some years ago that the square root of the intensities (A) of the infrared ring vibrations at *ca.* 1 600 cm^{-1} (ν_8) measured the π-electron transfer to or from the substituent in monosubstituted benzenes. These $A^{\frac{1}{2}}$ values formed the basis of a $\sigma_R{}^\circ$ scale for an extensive number of substituents. Some $A^{\frac{1}{2}}$ values[15,16] are listed in Table 1 and plots of these *versus* $\Sigma\Delta q_\pi$ again show deviations for π-electron-withdrawing groups at the 4-31G basis.

Another check is between the calculated values of the change in π-electron population at the *para*-carbon atom [Δq_π(*para*)] and the *para*-carbon-13 substitutent chemical shifts (SCS) in monosubstituted benzenes. Agreement is known[17] to be quite reasonable for calculations at the STO-3G basis set but, as shown in Figure 4, once again the values for the π-electron withdrawers are not well represented at the 4-31G level.

Overall then, we are left with no alternative but to conclude that the STO-3G basis set gives a better explanation of properties that are significantly influenced by π-electron transfer in these systems.

Table 3. Substituent constant $\sigma_R{}^\circ$

Substituent	$\Sigma\Delta q_\pi{}^a$	$\sigma_R{}^\circ$ (theor.)	$\sigma_R{}^\circ$ (lit.)
$NMe_{2(pl)}$	−129	−0.58	−0.53
$NHMe_{(pl)}$	−125, −125	−0.56	−0.52
$NH_{2(pl)}$	−119	−0.53	−0.47
$NH_{2(tet)}$	−74	−0.32	
$NHOH_{(pl)}$	−126, −127	−0.57	−0.22
$NHOH_{(tet)}$	−66, −65	−0.27	
$NHNH_{2(pl)}$	−154, −149	−0.69	−0.49
$NHNH_{2(tet)}$	−72, −78	−0.32	
NCO	−51	−0.20	−0.40
OMe	−96, −84	−0.39	−0.43
OH	−94, −86	−0.39	−0.40
F	−74	0.32	−0.34
C_6H_5	−5	0.01	−0.10
Me	−9	0.00	−0.10
Et	−9, −8	0.00	−0.10
Bu^t	−7	0.01	−0.13
CH_2CN	−6, −6	0.01	−0.09
CH_2OH	−7, −7	0.01	−0.06
CH_2F	−7, −7	0.01	
CHF_2	4, 10	0.07	
CF_3	11	0.09	0.10
C_2H_3	0	0.04	0.05
C_2H	3	0.05	−0.19
CHO	28, 26	0.17	0.24
COMe	25, 18	0.15	0.22
$CONH_2{}^+$	23, 16	0.14	0.13
CO_2Me^+	28, 26	0.17	0.16
CO_2H^-	29, 27	0.17	0.29
COF	30, 28	0.18	
COCN	34, 31	0.20	
$COCF_3$	33, 26	0.18	
CN	18	0.13	0.09
CNO	5	0.06	
NO	21, 23	0.15	0.25
NO_2	17	0.12	0.17
$NH_3{}^+$	−2	0.03	
$NMe_3{}^+$	−4	0.02	
$CO_2{}^-$	−4	0.02	
O^-	−446	−2.1	

[a] In 10^3 e. [b] Values for non-polar solvents.[15]

Redefinition of the Theoretical Scale of $\sigma_R{}^\circ$ Values.—Accordingly, we wished to redefine the theoretical $\sigma_R{}^\circ$ scale[4] using results at the STO-3G//STO-3G rather than at the 4-31G//4-31G basis set. We have earlier shown[3] that the π-electron transfer to or from the substituent in substituted ethylenes is an excellent linear function of the transfer in the corresponding substituted benzenes, provided the basis set used is the same. Acordingly, we have calculated such π-electron transfers for an extensive series of monosubstituted ethylenes and the results are shown in Table 3. In the case of non-symmetrical substituents, both *cis* and *trans* forms are possible and results for both structures are given. (In the determination of the $\sigma_R{}^\circ$ values, there results are averaged.) We restricted the calculations to substituents containing only H and elements in the first major row, because of the deficiencies in minimal basis sets for higher atoms.

The calculated $\Sigma\Delta q_\pi$ values were then correlated with literature $\sigma_R{}^\circ$ values for substituents NMe_2, OMe, F, Me, CN, CF_3, COMe, and NO, as previously.[3] This led to equation (3)

$$\sigma_R{}^\circ = 4.8\Sigma\Delta q_\pi + 0.04 \qquad (3)$$

with a correlation coefficient of 0.982. In turn, this equation was used to derive the new scale of theoretical $\sigma_R{}^\circ$ values given in Table 3. Experimental values are also listed for comparison. The $\Sigma\Delta q_\pi$ values can also be compared with the recently defined σ_R values. Here, equation (4) is derived with a correlation coefficient of 0.985.

$$\sigma_R = 4.9\Sigma\Delta q_\pi + 0.03 \qquad (4)$$

Conclusions.—The results presented here suggest that calculation of π-electron transfers at the minimal basis STO-3G level are more in proportion to related experimental data than are those at the 4-31G level. This is likely to arise from fortuitous cancellation of errors at the lower level but, nevertheless, is a useful guide. The theoretical scale of $\sigma_R{}^\circ$ reported should provide a guide to experimental effects by substituents for which these are not well defined.

Acknowledgements

We are grateful to the Australian Research Grants Scheme for financial assistance.

References

1 W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, '*Ab Initio* Molecular Orbital Theory,' Wiley, New York, 1986.
2 E. R. Davidson and D. Feller, *Chem. Rev.*, 1986, **86**, 681.
3 S. Marriott and R. D. Topsom, *J. Mol. Struct.*, 1984, **106**, 277.
4 S. Marriott and R. D. Topsom, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1045.
5 S. Marriott and R. D. Topsom, *Aust. J. Chem.*, 1986, **39**, 1157.
6 S. Marriott, A. Silvestro, R. D. Topsom, and C. W. Bock, *J. Mol. Struct.*, 1987, **151**, 15.
7 S. Marriott, R. D. Topsom, C. B. Lebrilla, I. Koppel, M. Mishima, and R. W. Taft, *J. Mol. Struct.*, 1986, **137**, 133.
8 J. S. Binkley, M. Frisch, K. Raghavachari, D. De Frees, H. B. Schleyer, F. Fluder, R. Seeger, and J. A. Pople, 'Gaussian-82 Release A,' Department of Chemistry, Carnegie Mellon University, Pittsburgh, 1982.
9 J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.
10 S. Marriott and R. D. Topsom, *J. Mol. Struct.*, 1984, **110**, 337.
11 R. S. Mulliken, *J. Chem. Phys.*, 1955, **23**, 1833, 1841, 2338, 2343.
12 R. W. Taft and R. D. Topsom, *Prog. Phys. Org. Chem.*, 1987, **16**, 1.
13 S. W. Benson, F. R. Cruikshank, D. H. Golden, G. R. Haugen, H. E. O'Neil, A. S. Rogers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279.
14 J. Bromilow, R. T. C. Brownlee, V. O. Lopez, and R. W. Taft, *J. Org. Chem.*, 1979, **44**, 4766.
15 A. R. Katritzky and R. D. Topsom, *Chem. Rev.*, 1977, **77**, 639.
16 R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Am. Chem. Soc.*, 1968, **90**, 1757.
17 W. J. Hehre, R. W. Taft, and R. D. Topsom, *Prog. Phys. Org. Chem.*, 1976, **12**, 159.

Received 9th February 1987; *Paper* 7/230