Pure & Appl. Chem., Vol. 62, No. 3, pp. 463–466, 1990.
Printed in Great Britain.

NMR studies of bond-orders

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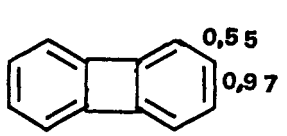
ABSTRACT - Allylic/*ortho*-benzylic interproton coupling constants involving a methyl group, i.e. $^4J_{Me-C\equiv\equiv C-H}$ henceforth designated as JoB, correlate well[1] with mobile bond-orders calculated in a number of ways in a representative series of hydrocarbons. Moreover, JoB is essentially independent of ring size and varies little with substituents in the conjugated systems studied[2]. Thus JoB appears to be a useful parameter for the study of mobile bond-orders and this work is concerned with applications to simple heterocyclic systems, biphenylene, 1,6-methano[10]annulene, azulene, quinones, the Mills-Nixon effect, fulvenes, porphyrins, sterically distorted benzenes, and electronically distorted benzene derivatives and heteroaromatics.

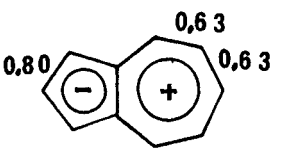
INTRODUCTION - We have recently[1] established that in a basic series of hydrocarbons including propanic single bonds of fixed geometry, cycloalkenes, benzene and 15 derivatives of simple polynuclear aromatic systems containing only six-membered rings, JoB correlates well with either the Pauling bond-orders or the squares of the SCF MO bond-orders. While it is easy to use JoB as a semiquantitative measure of bond-orders in other systems, we wish to show in this preliminary study that interesting insights into electron distributions in conjugated systems can be obtained by the JoB method without resorting to use of equations obtained from the above correlations.

HETEROAROMATIC SYSTEMS - JoB values for 20 methyl derivatives of simple heteroaromatic systems (furan, thiophene, pyridine, quinoline, pyridine oxide, pyrazole, pyridazine, pyrimidine, 2-pyridone and indole) correlate reasonably well with the squares of the relevant mobile bond-orders calculated by the SCF MO method, which however appears to overestimate delocalization in furan and underestimate delocalisation in 2-pyridone.

SOME POLYNUCLEAR AROMATICS - The values for JoB in biphenylene shown in structure (1) clearly confirm the radialene-like electron distribution. Similarly the values for JoB in azulene (2) are in accord with the accepted redistribution of π-electrons from the seven-membered ring to the five-membered ring. However the apparently equal bond-orders of C2-C3 and C3-C4 bonds in 1,6-methano[10]annulene (3) is contrary to expectations from the relevant bond lengths[3].



(1)



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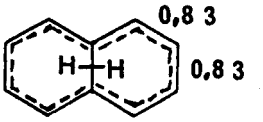
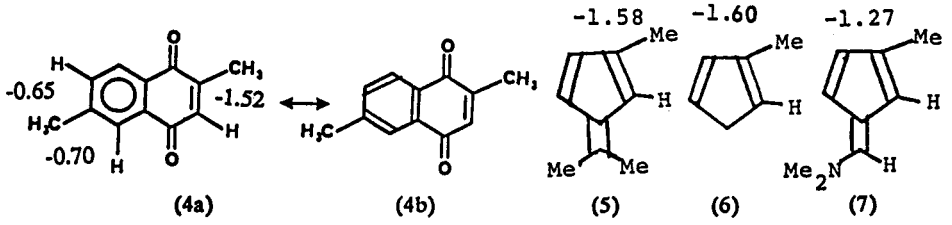


(3)

QUINONES - The JoB values in 11 derivatives of *ortho*- and *para*-benzoquinones correlate well with the SCF MO bond-orders, but more significant is the insight

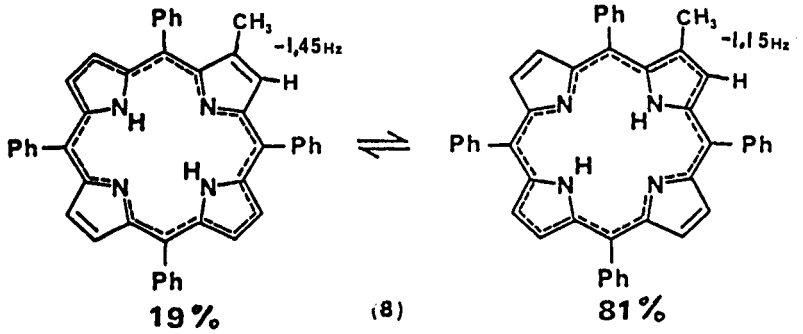
that benzene rings annelated to either *ortho* or *para* quinone rings remain essentially fully delocalised. Thus the intuitively attractive Valence-Bond structures such as (4b) contribute little to the electronic structure of 1,4-naphtoquinones which are best represented by VB structures such as (4a).



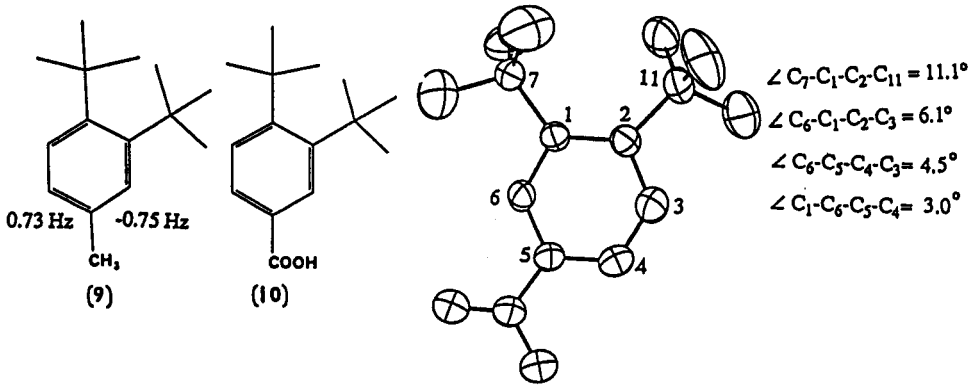
THE MILLS-NIXON EFFECT - The values of JoB in methyl substituted benzo*cyclo*propene, benzo*cyclo*butene, indane and tetralin show no evidence for bond-fixation as required by the existence of a ground-state Mills-Nixon effect.

FULVENES- The JoB/bond-order correlation permits us to investigate the contribution of *cyclo*pentadienyl-type electron distribution in fulvenes. It can be seen by comparison of the JoB values in a methylfulvene (5) with the reasonable model compound (6) that such contribution must be minimal, but the incorporation of a π-electron donor in the exocyclic portion (7) does increase it significantly.

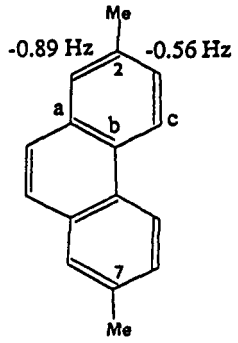
PORPHYRINS - The tetraphenylporphyrin (8) exists as a mixture of two tautomers[4], whose NMR parameters can be obtained independently from suitable experiments[4]. It can be seen that the double bonds *outside* the [18]annulene aromatic ring behave as separate double bonds and that the bonds at the heads of the pyrrolic fragments *inside* the [18]annulene aromatic ring have high electron densities.



DISTORTED AROMATIC RINGS-Sterically induced bending of aromatic rings would be expected to affect the overlap of p-orbitals and hence bond-order and aromatic properties. However it has been proposed[5] that the p-orbitals can adjust to the non-planarity of the σ-framework and thus maintain overlap. It can be seen that JoB in 2,3-di-*tert*butyltoluene (9) is identical to that in toluene[1] (0.75Hz).We have also prepared the corresponding crystalline benzoic acid (10) and determined its structure[6] by X-ray crystallography. Making the reasonable assumption that the skeletal distortions in (9) and (10) are the same it can be seen that the significant distortions in an *ortho*-di-*tert*butylbenzene derivative are not accompanied by changes in bond-order.

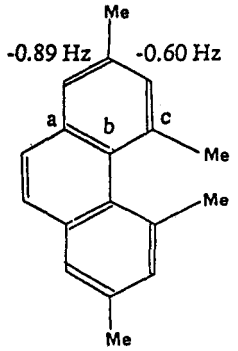


Assuming in an analogous manner that the skeletal distortions in 2,7-dimethylphenanthrene (11) are the same as in phenanthrene[7] and those in 2,4,5,7-tetramethylphenanthrene (12) are the same as in 4,5-dimethylphenanthrene[8], it can be seen that the very significant additional ring-bending involved in changing from (11) to (12) is not accompanied by any significant changes in JoB and hence bond-order.
Even more dramatic are the results for a series of *para*-cyclophanes (13), where the angle α determined crystallographically varies between 9.00^0 for X=$-(CH_2)_4-$ and 14.9^0 for X= $CO-CH_2-CH_2-CO$[9] while JoB remains identical within the experimental error (-0.66Hz),which is also the exact value for the relevant JoB in 1,2,4-trimethylbenzene[2], a reasonable model for $\alpha=0^0$.The results for series as a whole thus appear to indicate that the bending of a benzene ring toward a boat configuration by up to 15^0 is not accompanied by any detectable change in bond-order.



Folding a-b-c = 1.1°

(11)



Folding a-b-c = 10.8°

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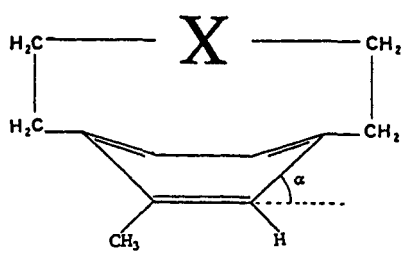
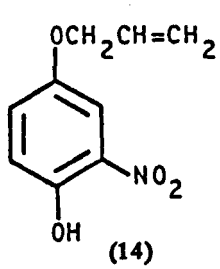
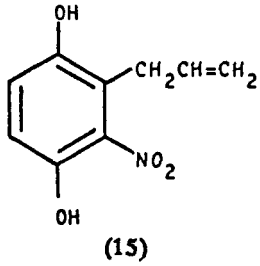


(13)

DISTORTION OF BENZENOID AND HETEROAROMATIC RINGS BY ELECTRONIC (SUBSTITUENT) EFFECTS - In contrast with the lack of sensitivity of JoB to steric distortion and with the well-documented general insensitivity of JoB to substituent effects[2], we have demonstrated much earlier[10] that in at least one case (2-nitro-*para*-cresol) a pair of *ortho*-related +R/-R substituents alters the values of JoB dramatically thus demonstrating that the benzene ring can have its electron cloud significantly localised in the ground state by appropriate substituents. This effect is numerically significant only for pairs of substituents with widely separated and opposing values of σ^R (OH/NO_2,NH_2/NO_2,F/NO_2,OH/COOH,NH_2/CN and OH/CN as *ortho* related pairs and -marginally- OH/NO_2 and NH_2/NO_2 as *para* related pairs) but may have chemical consequences.Thus the Claisen rearrangement of the allyl ether (14) leads exclusively to product (15) rather than (16) as predicted from the values of JoB in 2-nitro-*para*-cresol (17)[10].



(14)



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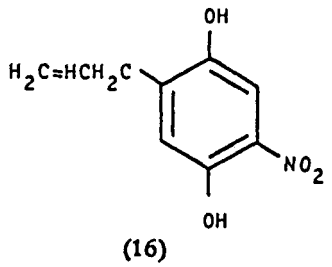

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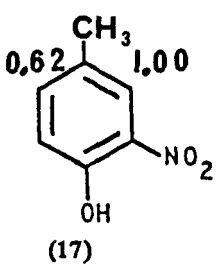
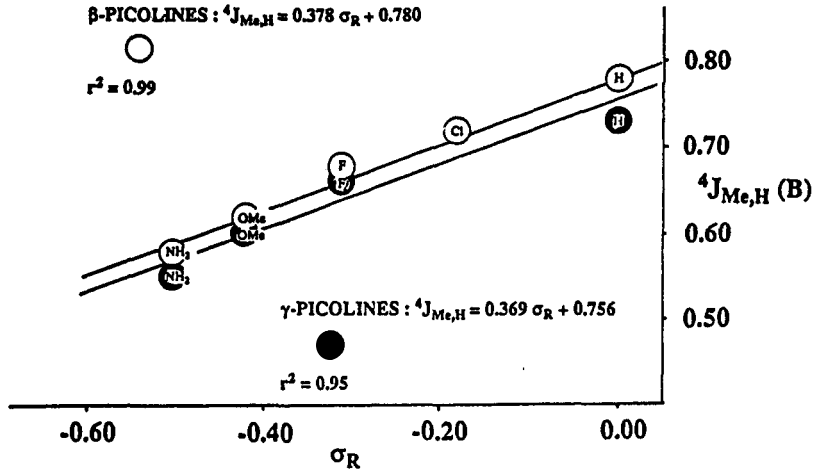


(17)

Analogous effects can be observed in pyrroles and pyrazoles suitably substituted with -R substituents but not with furans and thiophens.Substantial effects can be shown with β-

and γ-picolines and a plot of the bonds with *reduced* bond-order in both systems against the appropriate Hammett constants gives satisfactory straight lines.



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