interactions between ring substituents. Such an interpretation is consistent with the small values of the C5-C3-C5′ and C6-N-C6′ angles shown in Figure 2. A more detailed discussion of the structure of this and related compounds will be presented in a subsequent paper.

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A Reinvestigation of Nitrogen-15 Chemical Shifts of *para*-Substituted Nitrobenzenes[1]

Sir:

Recently several research groups[2-4] have determined ^{14}N chemical shifts for *para*-substituted nitrobenzenes, which deviate both in magnitude and sign from ^{15}N shifts for corresponding compounds reported 3 years ago.[5] These striking discrepancies prompted us to reinvestigate the substituent effects on the ^{15}N chemical shifts of nitrobenzenes because there seemed no obvious reason as to why the ^{14}N and ^{15}N shifts should differ widely.

Table I. Nitrogen Chemical Shifts of the Nitro Group in *para*-Substituted Nitrobenzenes[a]

Substituent	$^{15}N^b$	$^{14}N^c$	$^{14}N^d$	$^{14}N^e$	$^{15}N^f$
NH_2	4.4			−0.9	−0.3
$NHCOCH_3$	3.1				
H	0.0	0	0	0.0	0.0
OCH_3	4.4		−1	0.1	0.2
F	3.6				1.1
Cl	2.1				2.3
Br	1.3				2.7
CN	−2.6	6		3.8	3.3
CHO			4.5		
NO_2	−3.9		5	4.6	4.6
COOH		5			
Error	±0.2	±4	±1.4	±0.5	±0.2

[a] A positive value of the chemical shift indicates a shift upfield from nitrobenzene. The values in the last column were obtained for acetone solutions. Apart from this, the nmr measurements and the synthesis of the labeled compounds followed the previous description.[5] [b] Reference 5. [c] Reference 2. [d] Reference 3. [e] Reference 4. [f] This work.

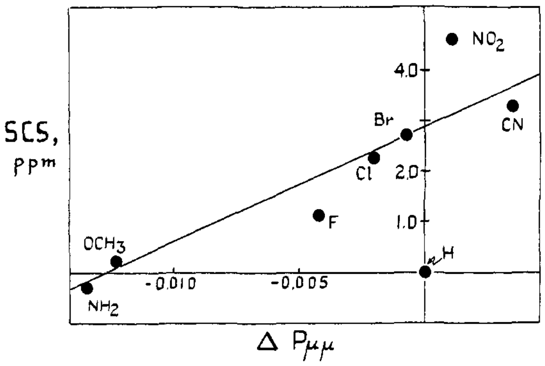

Figure 1. ^{15}N-substituent chemical shifts (SCS) as a function of changes in π-electron density, $\Delta_{\mu\mu}$, from simple HMO theory.

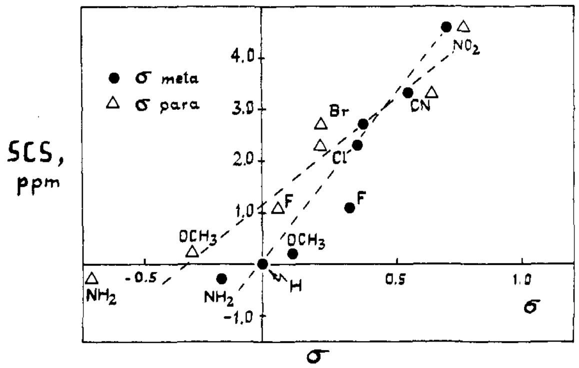

Figure 2. ^{15}N-substituent chemical shifts (SCS) and Hammett constants σ_m and σ_p.[7]

A summary of the results is presented in Table I. The substituent chemical shifts in the first column clearly differ both in sign and magnitude from the values found in four other investigations, which are largely consistent with one another. The only explanation we can offer for some of the erroneous shifts previously reported is that the field sweep was taken in the wrong direction.

The results indicate that the influence of the substituents on the ^{15}N chemical shifts of nitro groups is slightly different from their influence on ^{19}F chemical shifts.[6] Attempted correlations with the π-electron density, $P_{\mu\mu}$, on the nitrogen atom (Figure 1) or the π-bond order, $P_{\mu\nu}$, of the C-N or the N-O bonds show strong deviations from linearity. Especially striking is the reversal of *p*-dinitrobenzene and *p*-nitrobenzonitrile, as well as the fact that the best line does not go through the origin of the plot. Probably changes in π-electron density exert only a minor influence on the ^{15}N resonances of nitrobenzenes. This is also indicated by the correlation of ^{15}N shifts with the Hammett constants[7] σ_p and σ_m as shown in Figure 2. All substituents now fall in the right sequence, except for methoxy with σ_p. The fit with the σ_m seems better than for σ_p,

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[1] Supported by the National Science Foundation.

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in general agreement with Witanowski's observation[3] that the influence of *meta* and *para* substituents on nitrogen chemical shifts in nitrobenzene are nearly equal.

The bulk of the evidence now available suggests that the inductive effect may influence these nitrogen chemical shifts more than the mesomeric effect, a conclusion already reached by Witanowski.[8] The remaining effects which might be mesomeric in nature probably can be associated with the paramagnetic term arising from the mixing of the ground and excited electronic states.[9] Unfortunately, this is not easy to test because determination of the mean electronic excitation energy of the n → π* transition is difficult in nitrobenzenes because of masking by the α band.[10]

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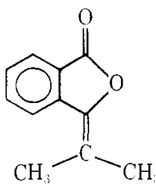
Photoaddition of Alcohols to Isopropylidinephthalide

Sir:

The photoaddition of alcohols to olefins in Markovnikov fashion to give ethers[1] seems to be limited to six- and seven-membered ring cases, and is usually accepted as proceeding through protonation of a highly strained *trans*-cycloalkane or orthogonal triplet. Additions of the oxygen of alcohols to the β position of α- and β-unsaturated ketones which have this double bond in a six-or seven-membered ring are also well documented,[2] and mechanistic similarity to the additions to cyclic olefins has been suggested.[2,3] The photoaddition of methanol to crotonic acid[4] is a well-reviewed counterexample to the necessity of having a cyclic double bond for the addition, but Kropp and Krauss reinvestigated this case and have convincingly shown[4] that there is no photoaddition of methanol here, and that acid-catalyzed reaction was probably responsible for the earlier result. More recently, however, the photoaddition of methanol to benzolylacrylic acid to give 2-methoxy-3-benzoylpropionic acid was reported.[5] We report here that alcohols add to the exocyclic double bond of isopropylidinephthalide (**1**),[6] a case of addition to a noncyclic double bond γ,δ to a carbonyl group. There is no chance of an ionic dark reaction being responsible here, since different products are formed under such conditions. Irradiation of **1** in methanol (1.4 × 10^{-2} *M*) for 14 hr with a 450-W Hanovia lamp converted about 39% of the starting material to the methanol adduct **2a**: nmr ($CDCl_3$) τ 1.8–2.6 (complex, 4 aromatic H), 4.25 (s, 1 methine H), 6.35 (s, 3 methoxyl H), 8.38 and 8.50 (2, s, 3 methyl H each); mass spectrum (15 eV) 206 (P, <1%), 191 (<1), 175 (12), 133 (100), 132 (20), 77 (28), 76 (20), all others <15%. The remainder of the photolysis mixture consisted of **1**, **3**,[7] and a small amount of dimeric material. Control experiments showed that **1** does not react with methanol in the dark, even upon 24-hr reflux, and that treatment with methanolic sulfuric acid, sodium hydroxide, and sodium methoxide gives only mixtures of **4** and **5**, and the **4**/**5** ratio varying from 2.1 to 3.9 depending upon conditions.



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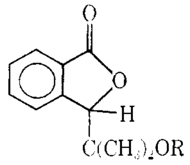
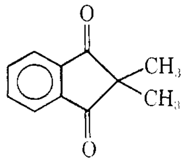


2a, R = CH_3
b, R = $C(CH_3)_2H$



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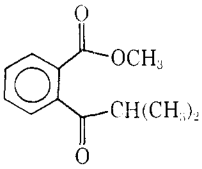

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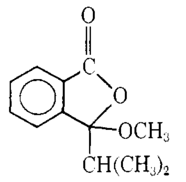

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Similarly, photolysis in 2-propanol gave **2b** as the major product: nmr ($CDCl_3$) τ 1.9–2.8 (complex, 4 aromatic H), 4.08 (s, 1 ring methine H), 5.72 (heptet, 1 isopropoxyl H), 8.40 and 8.52 (2 s, each 3 H), 8.70 and 8.73 (2, d, each 3 H); mass spectrum (15 eV) 234 (P, <1%), 133 (100), 132 (55), 77 (26), all others <15%.

Neither photoreduction nor radical addition of the alcohol occurs with **1**, even in 2-propanol, in contrast to the behavior of a steroidal acetylcyclopentene[8] and the sensitized behavior of several unsaturated acids.[9] Photolysis of **1** must lead to an intermediate with considerable polarization of the isopropylidine bond, possibly by protonation of the carbonyl carbon; enhanced basicities for some excited states are known.[10] We conclude that alcohol addition to olefins does not always require great strain in an orthogonal or *trans* intermediate if the double bond is conjugated with a carbonyl group.

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