Ionization Energies and Ring Orbital Interaction in Diarylmethanes and Diarylethanes

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(Z. Naturforsch. **27 a**, 534—536 [1972]; received 18 November 1971)

The ionization energies of a number of mono- and disubstituted diarylmethanes and diarylethanes were measured by electron impact mass spectrometry. No clear evidence of the homo conjugative phenomenon is obtained from this gas phase observable of the systems studied.

Introduction

The photoelectron energy spectra of diphenylmethane and diphenylethane were used to get information on the problem of homoconjugative effects in those systems. The similarity of their spectra to that of toluene suggested that if any non classical conjugation effect exists in the molecule, it is not strong enough to remove the degeneracy of the last four occupied π molecular orbitals[1].

However, other physico-chemical observables of these compounds have been interpreted with the intervention of such transannular effects[2-4].

In this paper we report the vertical ionization energies (or ionization potentials) of a number of mono and disubstituted derivatives of diphenylmethane and diphenylethane which were measured with the aim of contributing to this interesting problem. The substituent effect approach was choosen since it is one of the most powerful tools for the elucidation of structural problems.

Results and Discussion

It is well known that a linear correlation exists between the first ionization potential (I.P.) and σ_p^+-values[5]. This has been verified in many aromatic[5] and heteroaromatic[6] series, where the substituent is directly conjugated with the delocalized π system of the ring, which is the "extraction point". A similar correlation holds also in the case of the $NO_2-C_6H_4-CH_2-CH_2-C_6H_4-X$ derivatives (see Fig. 1 c). The correlation line lies about 0.25 eV

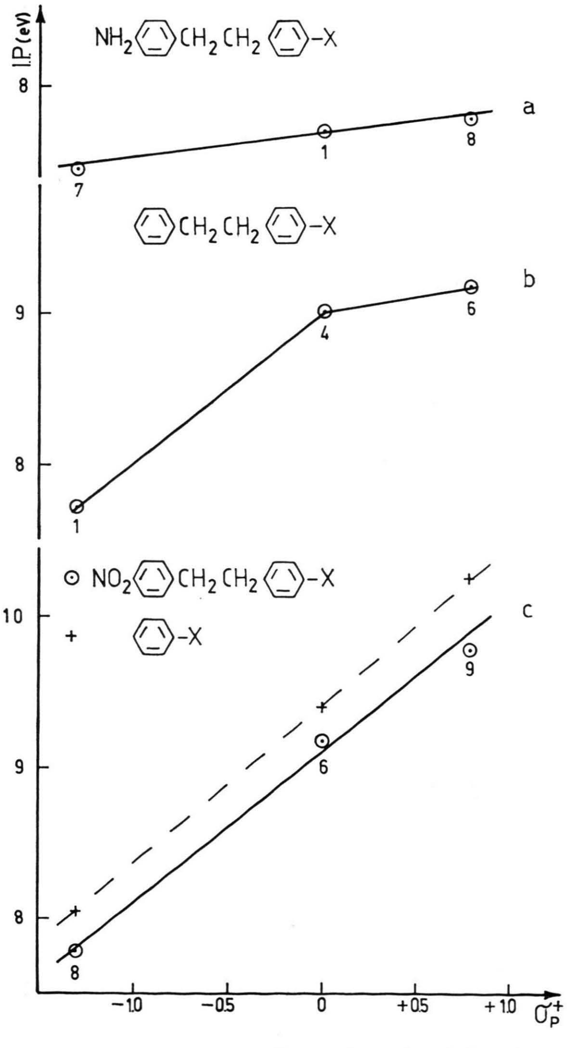

Fig. 1. Plot of diarylethanes I.P.'s vs. Brown's σ_p^+. The dashed line refers to vertical I.P. values from photoelectron spectroscopy (Ref. [8]). Brown's σ_p^+ values were taken from Ref. [9]. The numbers identify the substituents (see Table 1).

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below that of the C_6H_5-X derivatives in agreement with the fact that the diarylethane should resemble more the ethylbenzene than the benzene derivatives *.

The slopes of the two correlation lines are very similar.

Such correlation does not hold any more when the $C_6H_5-CH_2-CH_2-C_6H_4-X$ are considered (see Fig. 1 b). The slope of the line joining the points for $X=NH_2$ and $X=H$ is similar to that of the benzenes, but it is quite different from that of the line joining the points for $X=H$ and $X=NO_2$. When the $NH_2-C_6H_4-CH_2-CH_2-C_6H_4-X$ are considered, a still different behaviour is found: the I.P.'s are nearly insensitive to the substituent effects (see Fig. 1 a). A difference of 0.3 eV only is found between the compounds having $X=NH_2$ and $X=NO_2$. Such behaviour has to be compared with that of the $NH_2-C_6H_4-X$: a difference of about 1.5 eV is found [7] instead.

If we take as a limiting model that of two isolated benzenic rings not interacting at all, it is to be expected that:

1 – the energy required to remove the least firmly bound electron from the $NH_2-C_6H_4-CH_2-CH_2-C_6H_4-X$ is constant and equal to the value for the $NH_2-C_6H_4-$ moiety (the lowest possible);

2 – the first I.P.'s of the $C_6H_5-CH_2-CH_2-C_6H_4-X$ derivatives must increase on going from the NH_2 to the unsubstituted derivative. With withdrawing substituent X, the "extraction point" shifts on the unsubstituted benzene ring, since the energy necessary to remove one electron from this part of the molecule is now lower than that required to ionize an electron from the substituted ring; under this condition the plot of the I.P.'s vs. σ_p^+ must show a break at $X=H$;

3 – when the $NO_2-C_6H_4-CH_2-CH_2-C_6H_4-X$ derivatives are considered, the "extraction point" does not shift along the series, but remains on the C_6H_4-X part of the molecule, since the energy required to remove one electron from the $NO_2-C_6H_4$-part is always higher (except for the case of the $NO_2-C_6H_4-CH_2-CH_2-C_6H_4-NO_2$ where the two energies are equal). Under this condition a linear correlation between the I.P.'s and the σ_p^+, having a slope very near to that of the benzenes, must be found.

The results shown in Fig. 1 approximate this model, indicating therefore that the homoconjugative phenomenon [10] has negligible effect on the present observable. The slight deviation from the simple situation predicted by the above limiting case can be accounted for by an inductive or through bond [11] effect.

Similar arguments can be developed for the methane series (see Fig. 2), so that similar conclusions can be drawn also for the diarylmethanes.

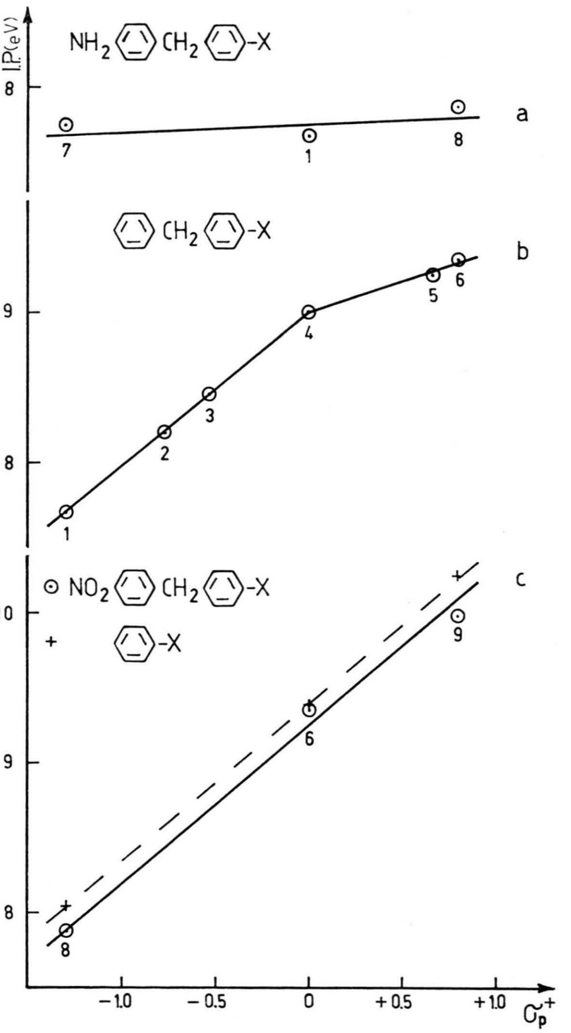

Fig. 2. Plot of diarylmethane I.P.'s vs. Brown's σ_p^+. The dashed line refers to vertical I.P. values from photoelectron spectroscopy (Ref. [8]). The σ_p^+ value for the OH group was taken from Ref. [12]. The numbers identify the substituents (see Table 1).

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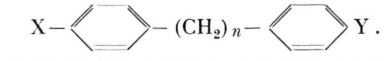
* For the comparison we have chosen the benzenes since the I.P. values for ethylbenzenes are not so reliable and self-consistent as those available for benzenes.

A support to this conclusion can be found from a comparison of the I.P. figures reported in Table 1. As a general trend, it is seen that the diarylethane derivatives show I.P.'s slightly lower than the corresponding diarylmethanes. Such behaviour can be interpreted as due, at least in part, to a greater inductive effect of the CH_2 chain in the ethane derivatives. By contrast, it cannot be based on a predominantly homoconjugative effect. For the series in which the homoconjugative effect is greater, one should find indeed higher I.P.'s when NO_2 groups are present (compounds No. 6, 8, 9 in the Table), while in the other cases (compounds No. 1, 2, 3, 4, 7) lower I.P.'s should be expected.

Table 1. Vertical ionization energies of diarylmethane and diarylethane derivatives (eV)



	Substituent		Diarylmethane	Diarylethane
No.	X	Y	(n=1)	(n=2)
1	NH_2	H	7.67	7.55
2	OCH_3	H	8.20	
3	OH	H	8.45	
4	H	H	9.00	9.00
5	CN	H	9.25	
6	NO_2	H	9.35	9.17
7	NH_2	NH_2	7.75	7.45
8	NH_2	NO_2	7.87	7.78
9	NO_2	NO_2	9.98	9.77

The present results are in agreement with those previously obtained by photoelectron spectrometry, so that, at least in the gaseous phase, the homoconjugative effect in the systems here studied, is negligible and, at most, of the order of magnitude of inductive effects.

Experimental

An Atlas CH_4 mass spectrometer was used for the measurements. The samples were introduced either through the gas inlet system or the direct insertion probe. Xe was used as standard. Some times, to check certain I.P. differences, two samples were calibrated one against the other. The I.P.'s were evaluated by Honig's method [13], the reproducibility being within ± 0.05 eV. For the other experimental conditions see Ref. [14]. The samples 8 [15] and 9 [16] and the 4-nitrodiphenylmethane [17] were prepared according to previously described procedures. The 4-nitrodiphenylethane was prepared by reducing the trans-4-nitrostilbene [18] with diimide generated from p-toluen-sulfonyl-hydrazine [19]. The compounds 1 and 7 were prepared by reducing the corresponding nitroderivatives; 2 and 3 were prepared from 1 following conventional methods. The compounds 4 were commercial samples.

Acknowledgment

This investigation was supported in part by a research grant from the "Consiglio Nazionale delle Ricerche Italiano". The authors wish to thank Prof. A. Foffani and Prof. G. Marino for the aid and encouragement given during the work.

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