Photoelectron Spectrum of Benzyne

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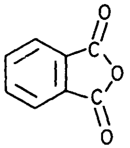
The u.v. photoelectron (UPE) spectrum of benzyne, prepared by flash vacuum thermolysis of phthalic anhydride or indantrione, is reported; bands corresponding to benzyne were not observed in the UPE spectra of the products from pyrolysis of iodobenzene, *o*-di-iodobenzene, or benzoyl bromide.

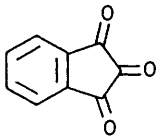
Benzyne [1,2-didehydrobenzene (**1**)] has been known for many years as an intermediate in reactions.[1] Its matrix-isolated i.r.[2] and gas phase u.v.[3] spectra have been reported but studies of its ultraviolet photoelectron (UPE) spectrum have not been published. We have now observed bands in the UPE spectra of the products from the flash vacuum thermolysis of phthalic anhydride (**2**) or indantrione (**3**) which, we believe, can be attributed to (**1**). These reactions are known[4] to generate (**1**) in good yield, together with oxides of carbon.

The materials used were commercial samples, distilled or recrystallized before use. The UPE spectra were measured on a home built spectrometer[5] with a 127° cylindrical analyser (see Turner[6]), samples being admitted to the target chamber through an electrically heated alumina capillary (maximum temperature 1200 °C).

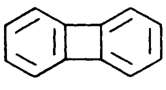
(**1**)



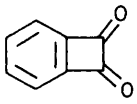
(**2**)



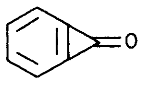
(**3**)



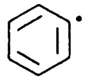
(**4**)



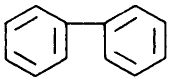
(**5**)



(**6**)



(**7**)



(**8**)

$H_2C{=}C{=}C{=}CH_2$

(**9**)

$H_2C{=}CH{-}C{\equiv}C{-}CH{=}CH_2$

(**10**)

Table 1. Vertical ionization potential (IP, eV) by photoelectron spectroscopy (PES).

PES of (**4**)[a]	PES of (**4**)[b]	New bands[c]	MNDO of (**1**)	MNDO of benzene
7.62	7.61	7.62	9.57a_2	9.39π
8.89	8.89	8.89	9.83b_1	12.48
9.68	9.63	9.15	9.93π	12.61π
10.10	10.08	9.24		
11.04	11.07	9.65		
		9.75		
11.50	11.45	9.87		
		10.11		

[a] Ref. 9. [b] This work at 1000 °C. [c] After pyrolysis of (2) or (3).

Calculations were carried out using the MNDO model[7] as implemented in the MOPAC program.[8] All geometries were fully optimized, using the procedures included in MOPAC, except when specific values were deliberately assigned to specific parameters. Ionization potentials (IP) were derived from orbital energies *via* Koopman's Theorem.

Under our conditions, (**2**) was not completely decomposed even at 1130 °C. However, the peaks corresponding to (**2**) became weaker and peaks corresponding to carbon monoxide, carbon dioxide, and biphenylene (**4**) appeared, together with three new bands in the low energy region, at 9.24, 9.75, and 9.87 eV, which we attribute to (**1**).

While the UPE spectrum of (**4**) has been reported,[9] we measured it again ourselves as a check, to make sure that the new bands were not due to it. Table 1 compares our IPs for (**4**) with the earlier values.

The thermolysis of (**3**) leads[4] to (**1**) *via* benzocyclobutendione (**5**), (**5**) being formed at lower temperatures. Under our conditions, the bands corresponding to (**3**) had disappeared completely at 1000 °C, bands corresponding to CO, (**5**), and (**1**) appearing in their place.

Figure 1 shows the spectra observed for (**2**) and (**3**) at 1100 °C. The fact that the same three bands were observed in both cases seems to leave little doubt that they correspond to (**1**). The only reasonable alternatives would be benzocyclopropenone (**6**) or phenyl radical (**7**). The former seems ruled out by failure to observe its formation in preparative thermolyses and by the near certainty that it must be more thermolabile than (**5**) and the latter by the intensities of the observed bands. While UPE spectra of simple alkyl radicals (ethyl, t-butyl, benzyl, allyl) have been observed[10] with our spectrometer, the signals from them were very weak, presumably owing to rapid secondary reactions of the radicals. Since (**7**) is even more reactive, any signal from it would be even weaker. Indeed, all our attempts to observe its UPE spectrum, using a variety of precursors, have failed. Note in this connection that our high temperature spectra invariably exhibited a very small peak at 9.15 eV (see Figure 1). This probably represents biphenyl (**8**), formed by dimerization of (**7**).

To check these conclusions, MNDO calculations were carried out for (**1**). The earlier report[11] of such calculations omitted orbital energies. Table 1 compares our calculated IPs with those attributed to (**1**), corresponding values for benzene being included for comparison. The results are consistent with our identification of the species from (**2**) or (**3**) as benzyne. The first two bands correspond to ionizations and the third to ionization from the in-plane pseudo-π MO. The degeneracy of the HOMO in benzene is removed in (**1**), as expected, because of the greater magnitude of the resonance integral for the short 'acetylenic' bond. Since the partial bond order of this bond in the A_2 MO is very small (1/12) and since the lengths of the other C–C bonds in (**1**) are similar to those in benzene, the first IPs of (**1**) and benzene are almost identical.

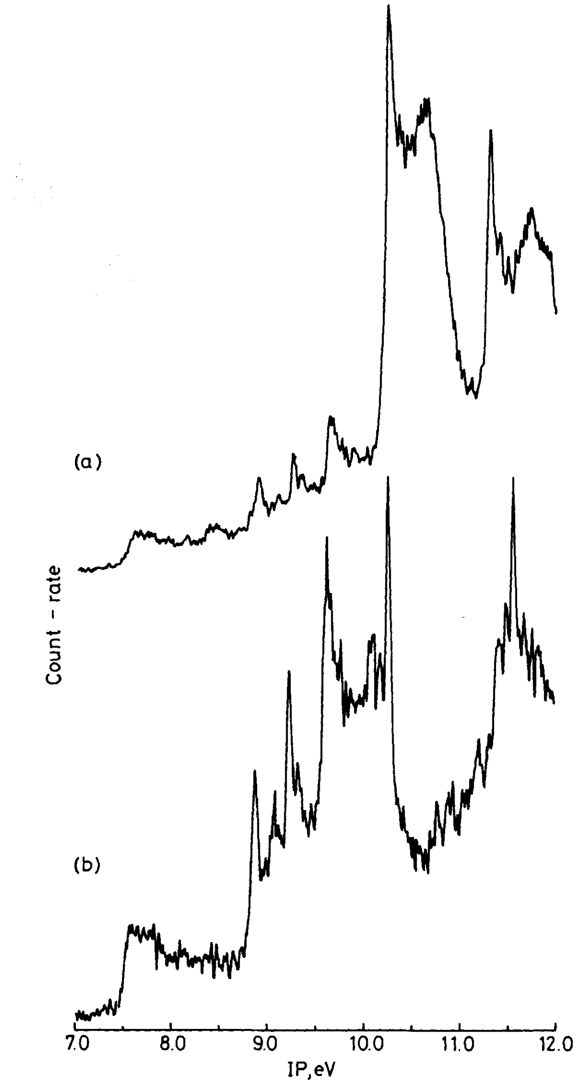


Figure 1. Photoelectron spectra at 1100 °C of (a) (**2**) and (b) (**3**).

As a further check, we carried out calculations for two other molecules with analogous orthogonal MOs, *i.e.* butatriene (**9**) and divinylacetylene (**10**). The calculations were carried out for equilibrium geometries, with the sp hybridized carbon atoms linear, and for bent geometries with the corresponding C–C–C bond angles the same as in (**1**). Calculations were also carried out for bent (**9**) with the central bond set to the same length (125.2 pm) as in (**1**). The results are summarized in Table 2. The second IP in each case corresponds to the isolated in-plane π-bond. The IPs calculated for (equilibrium) (**9**) agree well with experiment, while the second IP for (**9**), distorted to the geometry of (**1**), agrees well with the observed third IP of (**1**).

These results confirm our attribution of the observed bands to (**1**) and seem to establish their assignment. They also resolve a recent controversy concerning its structure. Some years ago Laing and Berry[12] claimed that the i.r. spectrum of (**1**) indicated a dienyne-like structure with alternating bond lengths. Calculations by a variety of procedures[13—15] have, however, predicted the 'acetylenic' bond to be much longer than a normal C–C triple bond and the other C–C bonds to be similar in length. The IP corresponding to the in-plane π-bond is much less than the values for normal C–C triple bonds, while the results in Tables 1 and 2 show it to be consistent with the calculated geometry. The near identity of the first IPs of (**1**) and benzene also indicates that the other C–C bonds in (**1**) cannot alternate significantly in length. Furthermore, MNDO calculations[16] suggest an alternative assignment of the i.r. bands which is also consistent with the calculated structure.

Table 2. Ionization potential (IP, eV) of (**9**) and (**10**).

PES of (**9**)[a]	MNDO of (**9**)	MNDO of (**9**) (bent 129°)	MNDO of (**9**) (bent 129°)[b]
9.30	9.01	9.22	9.02
9.98[d]	9.94[d]	9.59[d]	9.84[d]
11.78	12.34	12.53	12.50

PES of (**10**)[c]	MNDO of (**10**) (C_{2h})	MNDO of (**10**) (C_{2v})	MNDO of (**10**) (bent 129°)
8.71	8.98	9.06	8.95
9.97[d]	10.57[d]	10.59	9.86[d]
11.00	10.61	10.60[d]	10.69

[a] F. Brogli, E. Heilbronner, E. Kloster-Jensen, A. Schmelzer, A. S. Manocha, and J. A. Pople, *Chem. Phys.*, 1974, **4**, 107. [b] C(1)–C(2) = 1.252 Å. [c] F. Brogli, E. Heilbronner, J. Wirz, E. Kloster-Jensen, R. G. Bergman, K. P. C. Vollhardt, and A. J. Ashe, III, *Helv. Chim. Acta*, 1975, **58**, 2620. [d] Isolated in-plane π-orbital.

It seems surprising that the UPE spectrum of (**1**) has not been reported previously, given the ease with which (**1**) can be prepared from (**2**) or (**3**). The near identity of its first IP with that of benzene may perhaps have misled other workers. Under our conditions attempts to prepare (**1**) from other possible precursors (iodobenzene, *o*-di-iodobenzene,[17] benzoyl bromide) failed.

This work was supported by the Air Force Office of Scientific Research, the Robert A. Welch Foundation, and the National Science Foundation.

Received, 9th April 1985; Com. 474

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