286. *Dewar* Benzene and Some of its Derivatives. A Photoelectron Spectroscopic Analysis [1]

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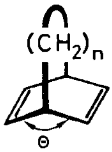
Summary. The near degeneracy of the two lowest ionization energies of *Dewar* benzene can be understood in terms of closely competitive 'through-bond' and 'through-space' interaction. Empirical, semiempirical, and open-shell *ab initio* procedures converge to require mutually consistent symmetry assignments.

Introduction. – The importance of *Dewar* benzene (**3**) derives from its structural relationship to benzene, from its simplicity, and from its symmetry. The first report of its successful synthesis [2] soon encouraged a rapidly growing number of theoretical investigations [3]. Experimental data have come much more slowly [4] and, even then, rarely in a form conducive to theoretical scrutiny. Such imbalance, we trust, may be somewhat relieved by this report of the He(I) photoelectron spectrum of *Dewar* benzene and of its analysis.

3

We shall find it particularly useful to regard **3** as the terminal member of the series of bridged bicyclic dienes, **I**(n), where n now equals zero. The photoelectron spectra of the higher members of this series follow a pattern that is quite easily understood – at least at the level of empirical HMO theory [5a, b]. As n increases from 1 to 4 and θ from 112° [6] to *ca.* 135°, 'through-space' interaction becomes



I(n)

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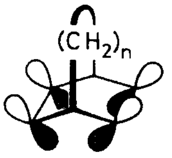
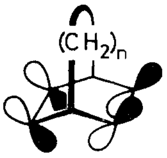
increasingly less important than 'through-bond' interaction [7]. As a result, between $n = 2$ and $n = 3$ $a_1(\pi)$ replaces $b_2(\pi)$ as the highest occupied molecular orbital. The energy gap between the two widens at both sides of this crossing point, monotonically so for increasing values of n [5].



$a_1(\pi)$



$b_2(\pi)$

As n decreases, however, we now find that the widening suddely collapses: from 0.85 eV in norbornadiene (**I**(1)) to 0.3 eV in *Dewar* benzene (**I**(0)). We shall, of course, still want to learn whether the 'natural order' — b_2 over a_1 — that was present in norbornadiene is retained. Is a new level crossing being approached or has it already been just achieved? Both empirical and semiempirical approaches will be used for this purpose.

More important, however, we will want to learn how the removal of the last bridging CH_2 group has affected the nature and the magnitude of 'through-bond' interaction. Recent applications of semiempirical SCF procedures [5c] now permit a more quantitative answer to such questions than was previously thought possible.

Finally, we shall want to protect any such level assignment from its inevitable reliance on *Koopmans'* theorem, the identification of ionization energies ($I_{v,j}$) with orbital energies ($-\varepsilon_j$). Since the limitations of the theorem are well known [8], we though it best also to complete an open shell STO-3G[9] *Hartree Fock* treatment of the radical cation **3**$^{+\cdot}$.

Results. – The He(I) photoelectron spectra of bicyclo[2.2.0]hexane [10] (**1**), of bicyclo[2.2.0]hex-2-ene [11] (**2**), of bicyclo[2.2.0]hexa-2,5-diene (*Dewar* benzene, **3**), of 1,2-*endo*,3-*endo*,4,5-*endo*,6-*endo*-hexamethyl-bicyclo[2.2.0]hexane (**4**) [12], of 1,2,3,4,5-*endo*,6-*endo*-hexamethyl-bicyclo[2.2.0]hex-2-ene (**5**) [12a], of 1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hexa-2,5-diene (hexamethyl *Dewar* benzene, **6**) [13], and of 1,2,3,4,5,6-hexafluorobicyclo[2.2.0]hexa-2,5-diene (**7**) [14] are illustrated in Fig. 1, 2 and 3. In addition, Fig. 3 includes the He(II) spectrum of **7**.

The spectra of **4**, **5** and **6** shown in Fig. 2 have been put at our disposal by *Brundle et al.* [15]. Our own spectrum of **6** agrees within the limits of error with theirs.

The He(I) spectrum of **7** has been previously recorded and discussed by *Delwiche & Praet* [16]. Their data are in complete agreement with ours, within the usual limits of error (*cf.* note at end of this paper).

Because of the unresolved vibrational fine structure of all the photoelectron bands, the observed band maxima ($I_{max,j}$) are identified with the vertical ionization energy ($I_{v,j}$) within the limits of experimental uncertainty. These are collected in Table 1. The labels ⓙ of the individual bands do not imply a correlation or assignment.

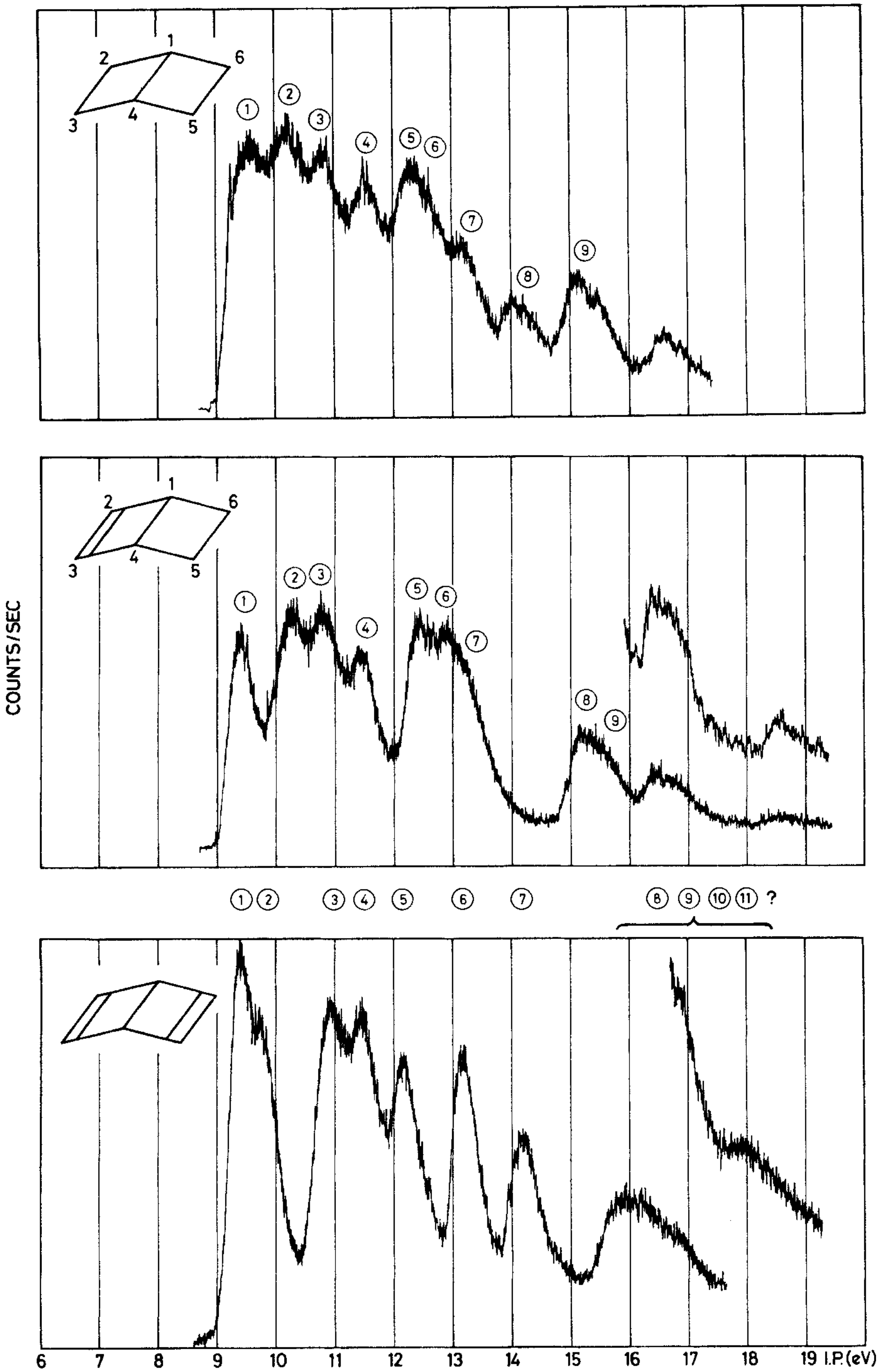


Fig. 1. *He(I) photoelectron spectra of* **1**, **2**, *and* **3**

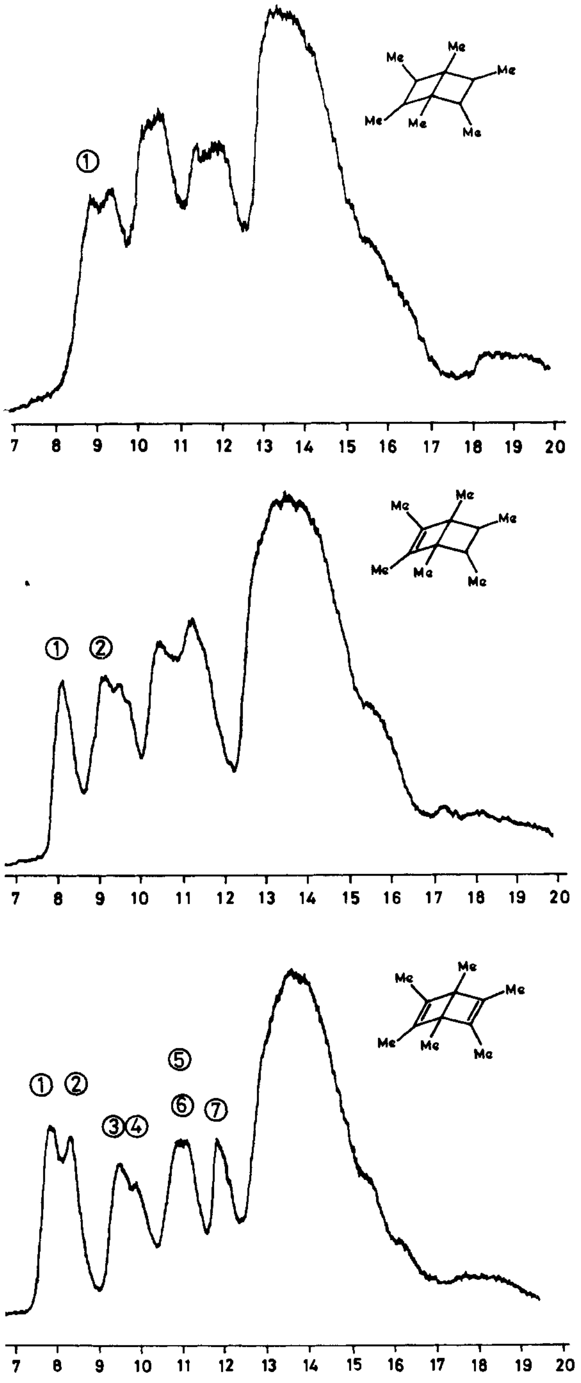


Fig. 2. *He(I) photoelectron spectra of* **4**, **5**, *and* **6**, recorded by *Brundle et al.* [15]

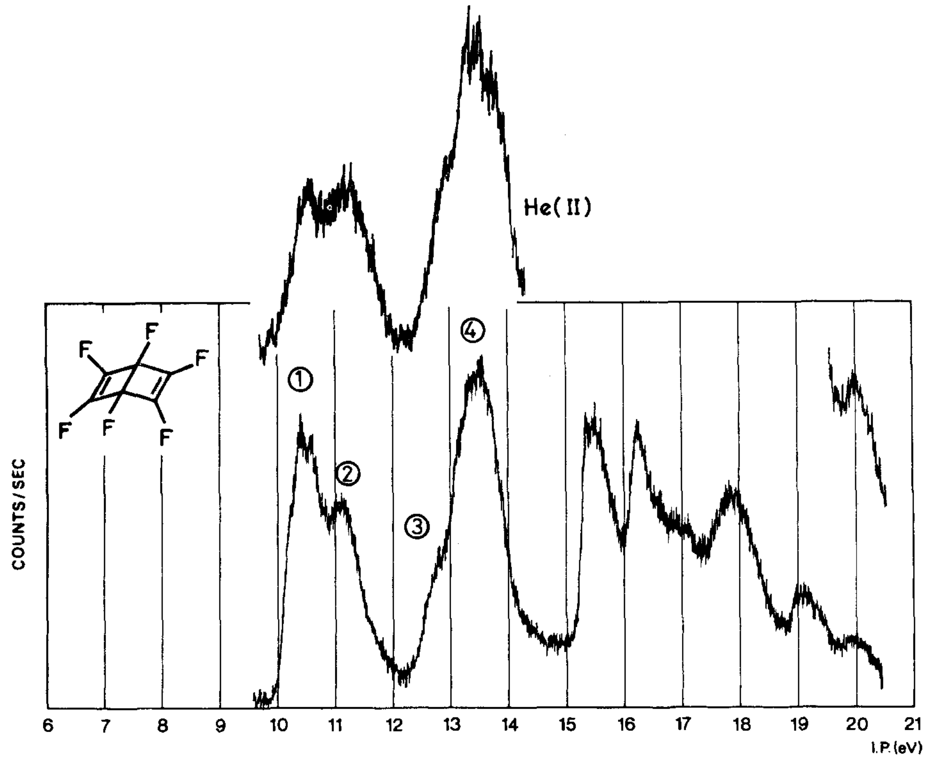
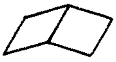


Fig. 3. *He(I) and He(II) photoelectron spectra of* **7**

Table 1. *Observed ionization energies* ($I_{v,j}$, eV)

Band j	1	2	3	4	5	6	7
①	9.6	9.4	9.4_0	8.8	8.1	7.8	10.4
②	10.2	10.3	9.7_0		9.1	8.3	11.1
③	10.8	10.8	10.9_5			9.5	12.9
④	11.5	11.4	11.5			9.9	13.5
⑤	12.3	12.4	12.2			10.8	
⑥	(12.3)	12.9	13.2			11.1	
⑦	13.2	(12.9)	14.2			11.8	
⑧	14.0	15.1	15.9				
⑨	15.1	15.5	(16.2)				
⑩			(16.6)				

In connection with the semiempirical and *ab initio* calculations, it was first essential to assign the molecular structural parameters of *Dewar* benzene. This was achieved by minimizing total energy with respect to all internal coordinates under C_{2v} symmetry by the MINDO/3 procedure [3k] [17]. The results are listed in the first column of Table 2. Since then, *Dewar et al.* have reported their own results using precisely the same procedure (column 2). The first experimental electron diffraction parameters have also become available (column 3) [4f]. Although we are at a loss to understand the small discrepancies between the first two columns, we think that both sets differ insignificantly from the third as well from those obtained by earlier *ab initio* calculations [3c,g]. The differences between the experimentally observed structural parameters of *Dewar* benzene, of hexamethyl *Dewar* benzene (**6**) [18] and of hexafluoro *Dewar* benzene (**7**) [19] are small but not entirely without their consequences.



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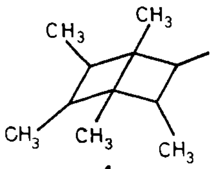

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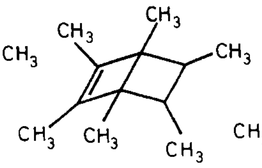

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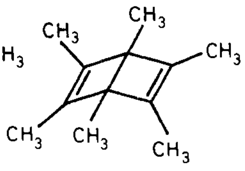

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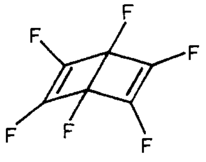

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Empirical Approaches. – It is important to recognize from the very beginning that these can never be as powerfully applied to *Dewar* benzene as they were to all higher members of the series **I**(n). So long as n was nonzero, the $(CH_2)_n$ bridge had always provided the structural opportunity for inserting a third double bond. Within the context of a simple HMO model, any such double bond contributes a new occupied π-orbital whose symmetry is unambiguously b_2 in C_{2v}. Then, after appropriate empirical correction to a common basis, the interaction of this new orbital with the original two could be analysed in a way that respected their original symmetry: $b_2(\pi)$ could interact, $a_1(\pi)$ could not. The assignments were quite unambiguous [5].

The structurally less conducive *Dewar* benzene requires much more data for any empirical approach. Those that we have obtained for this purpose are illustrated in Fig. 4. The observed $I_{v,j}$ have been equated to $-\varepsilon_j$. The orbital assignments of **1**, **2**, and **3** (derived from SPINDO calculations, more fully described in the next section) are introduced here merely to provide a common terminology. The correlation lines that join them follow the rule: $(a_1, b_2) \rightarrow a' \rightarrow (a_1, b_2)$ and $(a_2, b_1) \rightarrow a'' \rightarrow (a_2, b_1)$. Note that the two highest molecular orbitals of **3**, those of principal concern, have not yet been assigned.

Nevertheless, there should be no doubt but that those two are 'π bands'. Past experience consistently has shown that the successive introduction of unsaturation into a saturated unsubstituted hydrocarbon shifts the onset of the σ-bands by 0.6 to 0.7 eV for each double bond [20]. This is precisely what is observed in transforming **1** to **2** (0.7 eV) and **2** to **3** (0.6_5 eV).

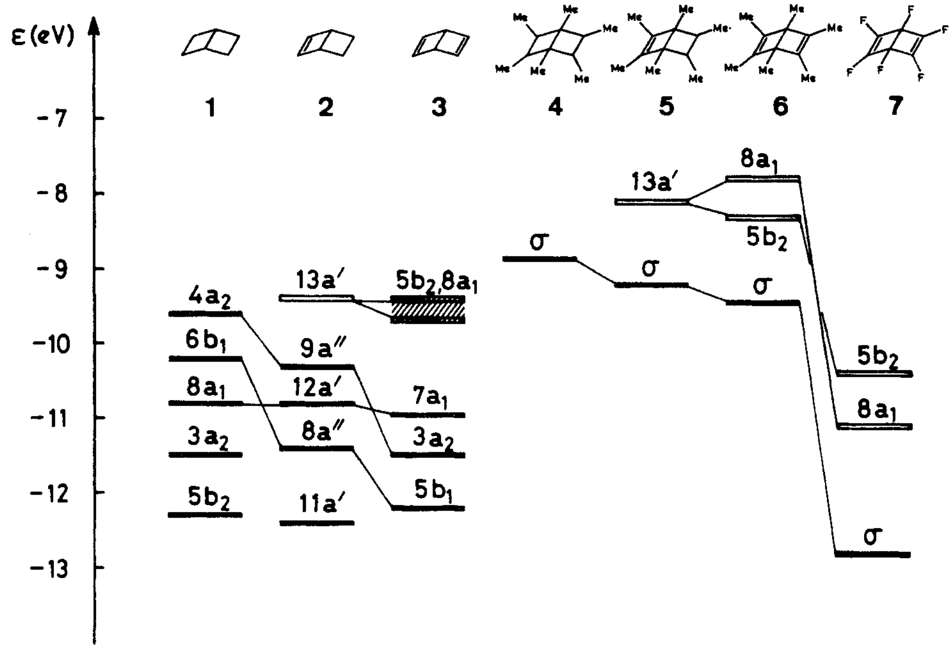


Fig. 4. *Orbital correlation diagram for the molecules* **1** *to* **7**. For clarity and convenience the orbital labels for **2** and **3** have been carried over to the substituted systems **5**, **6**, and **7**

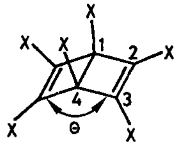
Similarly, the introduction of unsaturation into the hexamethylated series shifts the onset of its σ-bands by a consistent, if somewhat smaller amount: 0.3 eV for the first double bond and 0.4 eV for the second. The decreased magnitude of this shift results from the great increase in the number of interacting σ-orbitals which the six methyl groups provide.

To assess the influence of the methyl groups we compare each member of the unsubstituted series with its corresponding hexamethyl derivative: **1** with **4**, **2** with **5**, and **3** with **6**. The resulting identification of the π-bands in **5** and **6** (*cf.* Fig. 4) is then entirely consistent with past success in understanding the results of methyl substitution in simple ethylenes [21] [22] and benzenes [21] [23]. There, the experimental results could be simulated within the framework of a simple HMO model by introducing a perturbation $\delta\alpha \approx$ 1.0–1.2 eV for the *Coulomb* integral at the point of methyl substitution. At any level of unsaturation, methyl substitution lowers the ionization energy of a π-band more than it does the energy of a σ.

The observed π-bands of hexamethyl *Dewar* benzene (**6**) differ from those of the unsubstituted diene (**3**) in two significant ways. Both lead us to expect that **6** displays an 'inverted order' of assignment — $8a_1$ above $5b_2$ — as indicated in Fig. 4. For convenience we shall keep the symmetry labels and orbital numbering valid for **2** and **3** to characterize the orbitals in the substituted molecules **5**, **6**, and **7**.

First, the energy gap between the two bands is slightly if unmistakably greater in **6** than it is in **3**. Since the dihedral angle of **6** exceeds that of **3** (Table 2), we expect 'through-space' interaction to be less than in the unsubstituted hydrocarbon (**3**).

Table 2. *Theoretically and experimentally deduced structural parameters*



Parameter	Theoretical		Experimental		
	3, X = H		**3**, X = H [d])	**6**, X = CH_3 [e])	**7**, X = F [f]
$d(C_1–C_4)$ [a])	1.581 [b])	1.591 [c])	1.574	1.629	1.597
$d(C_1–C_2)$ [a])	1.524 [b])	1.522 [c])	1.524	1.523	1.503
$d(C_2–C_3)$ [a])	1.352 [b])	1.350 [c])	1.345	1.352	1.356
θ(dihedral)	120.6° [b])	118.3° [c])	117.3°	124.5°	115.3°

[a]) $\times 10^8$ cm^{-1}. [b]) This study. [c]) Ref. [3k]. [d]) Ref. [4f]. [e]) Ref. [18]. [f]) Ref. [19].

In addition, we expect the replacement of the two bridgehead C–H σ-orbitals at C(1) and C(4) by two C–CH_3 σ-orbitals to increase 'through-bond' interaction. Both considerations lead to the inverted order. It is amusing in this regard to note that *Goetz et al.* [24] reached precisely the opposite assignment by making the wholly unwarranted assumption that 'through-bond' interaction could entirely be neglected.

Second, we note that band ① of hexamethyl *Dewar* benzene (**6**) is significantly broader than band ②. Since we expect greater σ/π mixing in an orbital of a_1 rather than of b_2 symmetry, our assignment of ① to ionization from $8a_1$ is strengthened. Such an assignment was also chosen by *Schrader et al.* on the basis of CNDO calculations [25].

Our own view is that not one of these arguments is overly compelling. If we retain the assignment at this level of approximation, we do so principally to illustrate how the contrasting photoelectron spectrum of hexafluoro *Dewar* benzene can contribute to a first tentative assignment of orbital sequence in the unsubstituted hydrocarbon **3**.

Extensive investigation of the photoelectron spectra of fluorinated hydrocarbons has led to a set of empirical rules, collectively known as 'perfluoro effects' [26] [27]. In brief, fluorine substitution has been shown to have the following effects: a) Direct, in-plane substitution of a π-system, *e.g.* in hexafluorobenzene, leaves the π-ionization energies essentially unchanged but shifts σ-ionization energies to much higher values; b) Perfluorination of a non-planar unsaturated hydrocarbon will shift all ionization energies to higher values, the size of the shift depending on the π or σ character of the corresponding orbital. However, the rules governing these changes are far from being well understood [28].

While recognizing that noncoplanarity in **7** can introduce complications, we still think it reasonable to regard $5b_2$ as possessing more π-character than $8a_1$. If so, the greater energy gap between bands ① and ②, observed in the case of hexafluoro *Dewar* benzene (**7**), requires an assignment opposite to that required in the hexamethyl derivative (**6**): $5b_2$ is now above $8a_1$. (Again, we shall keep for **7** the orbital labels valid for the parent hydrocarbon **3**, rather than using $10b_2$ and $15a_1$).

As in the hexamethyl derivative, two consistent independent observations strengthen the assignment. Here it is band ②, rather than band ①, which is the broader one of the two, presumably because of greater σ/π mixing in $8a_1$.

In addition, although band ① is the more intense of the two in the He(I) spectrum, band ② becomes the more intense if He(II) radiation is used instead. Past experience has taught that ionization cross sections of π-orbitals decrease with increasing ionization energy [29]; those of fluorine 2p atomic orbitals with increasing ionization energy [30]. Clearly then, band ① behaves as if it were associated with an orbital having more π- and less fluorine lone-pair character than the one associated with band ②.

This is consistent with the assumption that band ① of **7** ought to be correlated with $5b_2$ rather than $8a_1$, because qualitative arguments suggest that $8a_1$ includes a greater contribution from the fluorine substitutents in positions 1 and 4.

This conclusion is fully supported by the very careful and detailed investigation of **7** by *Delwiche* & *Praet* [16], who derived the identical assignment on the basis of semiempirical calculations (*cf.* note at the end of this paper).

Assuming the reliability of these two deductions — $8a_1$ above $5b_2$ in the hexamethyl derivative (**6**) but below $5b_2$ in the hexafluoro (**7**) — what can we conclude about the corresponding assignment for the unsubstituted *Dewar* benzene? At this level of approximation, not very much indeed. Obviously, the two orbitals $8a_1$, $5b_2$ of **3** are so close in energy that an unambigous assignment is impossible. As a working hypothesis we shall therefore assume that the natural order prevails — $5b_2$ above $8a_1$ — as suggested by the SCF models to be discussed in the next paragraph.

Semiempirical SCF Approaches – Table 3 compares the observed $I_{v,j}$ with those that we have calculated by two semiempirical procedures — SPINDO [31] (column 3) and MINDO/3 [3k] [17] (column 4) — as well as by the STO-3G [32] *ab*

Table 3. *Observed ionization energies* ($I_{v,j}$) *and theoretically calculated orbital energies* ($-\varepsilon_j$) *of* Dewar *benzene* (**3**)

$\psi_j(C_{2v})$	$I_{v,j}$	$-\varepsilon_j^{\mathrm{SPINDO}}$	$-\varepsilon_j^{\mathrm{M/3}}$	$-\varepsilon_j^{\mathrm{STO\text{-}3G}}$	$-\varepsilon_j^{\mathrm{4\text{-}31G}}$ b)
$5b_2$	9.40	9.78	9.35 a)	7.81	9.1
$8a_1$	9.70	9.80	9.07 a)	7.89	9.6
$7a_1$	10.95	10.97	9.92	10.35	11.7
$3a_2$	11.5	11.26	9.94	10.80	12.3
$5b_1$	12.2	11.97	10.96	11.70	13.2
$4b_2$	13.2	13.32	11.76	12.98	14.4
$6a_1$	14.2	13.88	13.49	14.09	15.6
$3b_2$	15.9	15.68	15.18	16.54	18.0
$4b_1$	(16.2)	15.98	16.43 a)	16.93	18.2
$5a_1$	(16.6)	16.49	16.27 a)	17.36	18.8
$2a_2$	17.9	17.78	19.66	19.25	
$4a_1$	19.8	19.56	22.49	21.58	
$3b_1$	20.3	20.31	24.89	22.90	
$2b_2$	22.6	23.27	30.78	26.62	
$3a_1$		26.87	41.31	30.89	

a) Inversion of order. b) Recalculated from the results of ref. [3g].

initio procedure (column 5). Column 6 lists the remarkably accurate results which had earlier been obtained by *Newton et al.* [3g] through the 4-31G *ab initio* procedure using an extended *Gaussian* basis set. It is apparent that all of them, except only for MINDO/3, support the empirically comfortable assignment of $5b_2$ above $8a_1$.

This again [5c] illustrates the well known deficiencies of the MINDO model in its calculation of ionization energies and in its overemphasis on 'through-bond' interaction. The MINDO/3 results of Table 3 are perhaps somewhat better than those previously reported by *Jorgensen* & *Salem* [3f] at the MINDO/2 level. The $3a_2$ σ-orbital is no longer unrealistically placed between the two highest lying π-orbitals and the ionization energy has been raised from 8.77 to 9.07 eV (to 8.94 eV in the MINDO/3 results of [3k]). Nevertheless, MINDO/3 now incorrectly predicts that *Dewar* benzene should be easier to ionize than benzene (7.99 in MINDO/2, 9.22 in MINDO/3, and 9.24 in reality). Both MINDO procedures place $8a_1$ unrealistically higher than $5b_2$.

We had previously shown [33] that a more useful comparison with experiment could be obtained by linearly adjusting the calculated orbital energies, $\varepsilon_j^{\mathrm{SPINDO}}$ and $\varepsilon_j^{\mathrm{STO\text{-}3G}}$, to obtain more realistic predictions ($I_{v,j}^{\mathrm{SPINDO}}$ and $I_{v,j}^{\mathrm{STO\text{-}3G}}$ of equations (1) and (2)).

$$I_{v,j}^{\mathrm{STO\text{-}3G}} = 4.63\ \mathrm{eV} - 0.634\ \varepsilon_j^{\mathrm{STO\text{-}3G}}\ , \tag{1}$$

$$I_{v,j}^{\mathrm{SPINDO}} = -0.57\ \mathrm{eV} - 1.065\ \varepsilon_j^{\mathrm{SPINDO}}\ . \tag{2}$$

The linear parameters were obtained by a least-squares analysis of fifteen experimentally observed *vs.* theoretically calculated ionization energies of four different unsaturated hydrocarbons. For similar reasons, we now fit the ten pairs of $I_{v,j}$, $\varepsilon_j^{4\text{-}31G}$ values to the regression line (3) and find a correlation coefficient of 0.99! The results of such adjustment are illustrated in Table 4.

$$I_{v,j}^{4\text{-}31G} = (2.32 \pm 0.04)\mathrm{eV} - (0.757 \pm 0.013)\ \varepsilon_j^{4\text{-}31G}\ . \tag{3}$$

We prefer this procedure to that used by *Newton et al.* [3g], the simple multiplication of calculated $\varepsilon_{v,j}^{4\text{-}31G}$ by -0.9, following a suggestion of *Brundle et al.* [34]. Our experience is that any such parameters depend critically on the choice of basis functions. They ought not to be carried over from one *ab initio* calculation to another.

Table 4. *Observed ionization energies and linearly adjusted calculated orbital energies of* Dewar *benzene* (**3**)

$\psi_j(C_{2v})$	$I_{v,j}$	$I_{v,j}^{\mathrm{SPINDO}}$	$I_{v,j}^{\mathrm{STO\text{-}3G}}$	$I_{v,j}^{4\text{-}31G}$	$\psi_j(C_{2v})$	$I_{v,j}$	$I_{v,j}^{\mathrm{SPINDO}}$	$I_{v,j}^{\mathrm{STO\text{-}3G}}$	$I_{v,j}^{4\text{-}31G}$
$5b_2$	9.4_0	9.85	9.58	9.2	$4b_1$	(16.2)	16.45	15.36	16.1
$8a_1$	9.7_0	9.87	9.63	9.6	$5a_1$	(16.6)	16.99	15.64	16.5
$7a_1$	10.9_5	11.11	11.19	11.2	$2a_2$	17.9	18.37	16.83	
$3a_2$	11.5	11.42	11.48	11.6	$4a_1$	19.8	20.26	18.31	
$5b_1$	12.2	12.18	12.05	12.3	$3b_1$	20.3	21.06	19.15	
$4b_2$	13.2	13.62	12.86	13.2	$2b_2$	22.6	24.21	21.51	
$6a_1$	14.2	14.21	13.56	14.1	$3a_1$		28.05	24.21	
$3b_2$	15.9	16.13	15.12	15.9					

Other *ab initio* calculations [3c,e,f] of *Dewar* benzene are much less successful in anticipating the observed ionization energies.

The convenience of the SPINDO procedure (as well as its reasonable reliability) lends itself to a more penetrating analysis of these results in terms of the competing effects of 'through-space' and 'through-bond' interaction [5c]. The 15 occupied SPINDO molecular orbitals, φ_j, are first denoted as canonical molecular orbitals (CMO's) and distributed over the four irreducible representations of C_{2v} (4). (The discriminating plane of symmetry $\sigma(x,z)$ is that which contains the central C1–C4 bond.) The CMO's, φ_j, are labeled

Irreducible Representation	*Number of Orbitals*	*CMO's*	
A_1	6	$\varphi_1 \ldots \varphi_6$	(4)
A_2	2	φ_7, φ_8	
B_1	3	$\varphi_9 \ldots \varphi_{11}$	
B_2	4	$\varphi_{12} \ldots \varphi_{15}$	

within each irreducible representation in order of increasing energy: $\varphi_6 \equiv 8a_1$, $\varphi_8 \equiv 3a_2$, $\varphi_{11} \equiv 5b_1$ and $\varphi_{15} \equiv 5b_2$. Thus, φ_6 and φ_{15} are expected to exhibit the highest π-character.

Our next step is to transform these CMO's (φ_j) into localized molecular orbitals (LMO's, λ_j) using the intrinsic localization procedure of *Edmiston & Ruedenberg* [35]. Then, the LMO's are linearly combined into symmetry adapted localized orbitals (SLMO's, ϱ_j) which, for obvious reasons, distribute themselves over the four irreducible representations in the same way as the CMO's φ_j. Each SLMO ϱ_j is associated with a self-energy:

$$F_{\varrho,j,j} = \langle \varrho_j | \mathfrak{F} | \varrho_j \rangle \qquad (5)$$

where $\mathfrak{F}$ is the *Fock* operator of the system. In addition, there is a cross-term between the SLMO's ϱ_i, ϱ_j but only if ϱ_i and ϱ_j belong to the same irreducible representation;

$$F_{\varrho,i,j} = \langle \varrho_i | \mathfrak{F} | \varrho_j \rangle \qquad (6)$$

otherwise $F_{\varrho,i,j} = 0$. Since we shall be exclusively concerned with those orbitals which belong to A_1 and B_2, only the submatrices ($F_{\varrho,i,j}$) with i,j = 1–6 and i,j = 12–15 are included in Table 5. The (entirely qualitative) diagrams illustrate that ϱ_6 and ϱ_{15} are the linear in-phase and out-of-phase combinations of the LMO's $\lambda_a \equiv \pi_a$, $\lambda_b \equiv \pi_b$. The latter are the localized two-center π-orbitals of the two double bonds (7). We expect these to be the major contributors to the CMO's $\varphi_6 \equiv 8a_1$, $\varphi_{15} \equiv 5b_2$.

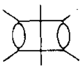
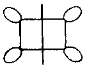
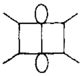
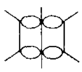
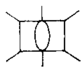
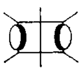
$$\varrho_6 = (\pi_a + \pi_b)/\sqrt{2}\,, \quad \varrho_{15} = (\pi_a - \pi_b)/\sqrt{2}\,. \qquad (7)$$

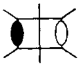
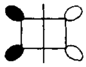
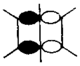
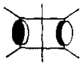
'Through-Space' Interaction. As before [5c], we define this to be $\langle \lambda_a | \mathfrak{F} | \lambda_b \rangle$: half the difference between the self-energies of the SLMO's ϱ_6 and ϱ_{15}. From Table 5, we obtain:

$$\langle \pi_a | \mathfrak{F} | \pi_b \rangle = 1/2(F_{\varrho,6,6} - F_{\varrho,15,15}) = -0.26 \text{ eV} \qquad (8)$$

'Through-space' interaction in *Dewar* benzene is thus almost exactly half of that calculated for norbornadiene (**I**(1)) whose two π-bonds are closer together and more inclined one to the other (dihedral angle 112° *vs.* 117° in **3**). Alternatively, this is the

Table 5. *Symmetry adapted localized molecular orbitals* (SLMO) *for* Dewar *benzene* (**3**) according to a SPINDO calculation, belonging to the irreducible representations A_1 and B_2. The matrix elements $\langle \varrho_i | \mathfrak{F} | \varrho_j \rangle = F_{\varrho,ij}$ are given in eV. The numbering of the ϱ_j corresponds to the convention defined in (4).

	ϱ_1	ϱ_2	ϱ_3	ϱ_4	ϱ_5	ϱ_6
A_1						
ϱ_1	–19.62	– 3.01	0.27	– 3.70	– 2.57	0.73
ϱ_2	– 3.01	–16.68	– 0.67	– 1.26	1.25	0.11
ϱ_3	0.27	– 0.67	–16.56	– 2.49	– 2.48	– 1.35
ϱ_4	– 3.70	– 1.26	– 2.49	–18.81	– 4.96	1.33
ϱ_5	– 2.57	1.25	– 2.48	– 4.96	–15.28	– 0.10
ϱ_6	0.73	0.11	– 1.35	1.33	– 0.10	–10.63

	ϱ_{12}	ϱ_{13}	ϱ_{14}	ϱ_{15}
B_2				
ϱ_{12}	–19.22	– 3.01	– 3.95	0.45
ϱ_{13}	– 3.01	–16.58	– 0.88	0.15
ϱ_{14}	– 3.95	– 0.88	–16.14	– 1.02
ϱ_{15}	0.45	0.15	– 1.02	–10.11

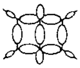
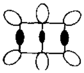
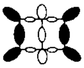
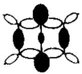
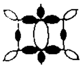
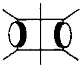
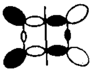
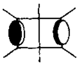
magnitude of 'through-space' interaction that would be expected in a hypothetical cyclohexa-1,4-diene with a dihedral angle of about 150°.

The orbital energies, $\varepsilon(5b_2)$ and $\varepsilon(8a_1)$ of the CMO's $\varphi_{15} \equiv 5b_2$ and $\varphi_6 \equiv 8a_1$ are both almost degenerate (–9.78 and –9.80 eV in the SPINDO model) and quite significantly higher than the corresponding self-energies of the SLMO's ϱ_{15} and ϱ_6 ($F_{\varrho,15,15} = -10.11$ eV, $F_{\varrho,6,6} = -10.63$ eV). From this it follows that 'through bond' interaction must be substantial in $5b_2$ as well as in $8a_1$.

'Through-Bond' Interaction. To assess which of the σ-SLMO's contribute most to this kind of interaction, we transform the SLMO's (ϱ_j) into precanonical molecular orbitals (PCMO's, ψ_j). This is achieved by a unitary transformation which diagonalizes only the $j = 1$ to 5 block of the A_1 submatrix of Table 5 and only the $j = 12$ to 14 block of the B_2 submatrix. All interaction terms within each of these two blocks — among the PCMO's ψ_1 to ψ_5 and among the PCMO's ψ_{12} to ψ_{14} — then vanish. The only nonzero cross-terms are those which link the PCMO's to the SLMO's ϱ_6 and ϱ_{15}. These cross-terms, the self-energies of the PCMO's ψ_j, and their qualitative diagrams are illustrated in Table 6.

Within the validity of a second-order perturbation treatment, the magnitude of each PCMO contribution to 'through-bond' interaction will vary as the square of the cross term. It will also vary inversely with the difference in self-energies. Within A_1, the first factor strongly mixes ψ_4 into ϱ_6 ($F_{\psi,4,6} = 1.23$ eV); the second factor strongly mixes in ψ_5 ($F_{\psi,5,5} = -10.85$, $F_{\psi,6,6} = -10.63$). All other PCMO's contribute much less. Within B_2, *all* of the cross-terms are quite small relative to the magnitude of self-energy differences. Thus, as we anticipated from the very start, $\varphi_{15} \equiv 5b_2$ is much more of a purely π-CMO than is $\varphi_6 \equiv 8a_1$.

Table 6. *Precanonical orbitals* ψ_j *of* Dewar *benzene* (**3**), according to a SPINDO calculation, belonging to the irreducible representations A_1 and B_2. The matrix elements $\langle\psi_i|\mathfrak{F}|\psi_j\rangle = F_{\psi,ij}$ are given in eV.

	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	$\psi_6 \equiv \varrho_6$
A_1						
$\langle\psi_i|\mathfrak{F}|\psi_i\rangle$	−26.82	−16.29	−19.49	−13.49	−10.85	−10.63
$\langle\psi_i|\mathfrak{F}|\psi_6\rangle$	0.89	− 1.06	− 0.79	1.23	− 0.39	
	ψ_{12}	ψ_{13}	ψ_{14}	$\psi_{15} \equiv \varrho_{15}$		
B_2						
$\langle\psi_i|\mathfrak{F}|\psi_i\rangle$	−23.27	−15.61	−13.05	−10.11		
$\langle\psi_i|\mathfrak{F}|\psi_{15}\rangle$	− 0.08	0.62	− 0.94			

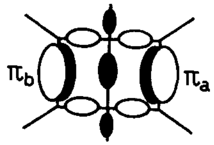
A more quantitative assessment is best achieved by diagonalizing the complete A_1 and B_2 matrices of the ψ_j. This leads back to the CMO's φ_j.

$$8a_1 \equiv \varphi_6 = 0.046\,\psi_1 - 0.145\,\psi_2 - 0.072\,\psi_3 + 0.294\,\psi_4 - 0.322\,\psi_5 + 0.884\,\varrho_6\,, \quad (9)$$

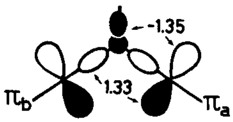
$$5b_2 \equiv \varphi_{15} = -0.006\,\psi_{12} + 0.102\,\psi_{13} - 0.274\,\psi_{14} + 0.956\,\varrho_{15}\,. \quad (10)$$

Alternatively, 'through-bond' contributions can be recognized by expressing (9) and (10) in terms of the SLMO's of Table 5 as illustrated in (11) and (12). Beneath each such equation, the diagrams IIa, IIb, IIIa and IIIb illustrate the phase relationships between the different SLMO's which contribute most to the two CMO's of principal concern.

$$8a_1 \equiv \varphi_6 = 0.032\,\varrho_1 - 0.087\,\varrho_2 - 0.192\,\varrho_3 + 0.325\,\varrho_4 - 0.295\,\varrho_5 + 0.884\,\varrho_6\,, \quad (11)$$

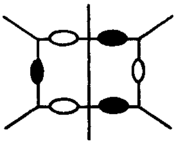


IIa

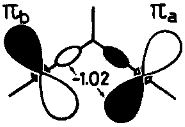


IIb

$$5b_2 \equiv \varphi_{15} = 0.155\,\varrho_{12} - 0.016\,\varrho_{13} - 0.248\,\varrho_{14} + 0.956\,\varrho_{15}\,. \quad (12)$$



IIIa



IIIb

It is apparent from equation (11) that ϱ_1 and ϱ_2 contribute little to $8a_1$. Diagrams IIa and IIb therefore include only ϱ_3, ϱ_4, ϱ_5, and ϱ_6. For similar reasons (equation 12), ϱ_{13} has been omitted from IIIa and IIIb. In addition, ϱ_{15} was omitted from IIIa in the interests of clarity.

The numbers included illustrate the principal interactions, more precisely the SLMO cross-terms of Table 5 (in eV). In 8 a_1, these link ϱ_6 with the C–H bridgehead orbital (ϱ_3, -1.35) but also with the upper and lower C–C σ-orbital (ϱ_4, $+1.33$). (It should be remembered that the cross-terms included in the diagrams of the canonical orbitals (11) and (12) refer to the phases of the SLMO's ϱ_i as defined in Table 5 and not to the phases of the ϱ_i in the linear combinations (11) and (12)).

Note that this latter interaction is very largely due to those C–C σ-bonds which are more remote from each of the two π-bonds — a phenomenon previously recognized in the higher members of the series **I**(n) [5c]. Finally, an entirely analogous interaction (of ϱ_{15} with ϱ_{14}, -1.02) is the principal contributor to 'through-bond' interaction in 5 b_2.

The central C_1–C_4 σ-orbital, ϱ_5, plays a curious role. For symmetry reasons, it cannot at all contribute to 5 b_2; its contribution to 8 a_1 (*cf.* equation 11) is obviously substantial. *Schrader et al.* [25] had indeed attributed a key role to this orbital in rationalizing their assignment of 8 a_1 over 5 b_2 in hexamethyl *Dewar* benzene (**6**). Recognizing the abnormally low C(1)–C(4) stretching force constant, these authors had assumed a correspondingly high σ-level to be the principal source of 'through-bond' interaction. They also suggested the alternative description: 'indirect interaction through space'.

Although we agree with these authors' assignment (now more reliably supported by SPINDO calculations), we cannot at all agree with their explanation. A glance at diagram IIb should immediately persuade the reader that it cannot be correct; ϱ_5 is virtually orthogonal to ϱ_6. Table 5 reveals the magnitude of the cross-term as merely -0.10 eV; the energy gap ($F_{\varrho,5,5} - F_{\varrho,6,6}$) is fully 4.65 eV!

The resolution of the apparent contradiction is also apparent from Table 5. Although ϱ_5 can hardly interact directly with ϱ_6, it interacts quite efficiently with all of the other SLMO's and, in particular, with ϱ_3 and ϱ_4. These last two, then, are the principal 'relay orbitals' for 'through-bond' interaction.

An Open-Shell Calculation. – The preceding dissection of the SPINDO results into 'through-space' and 'through-bond' contributions ought to be rather insensitive to any of the small quantitative deficiencies of such a semiempirical procedure. Unfortunately, the same cannot be said for its orbital assignment: 5 b_2 above 8 a_1 by only 0.02 eV. Any realistic evaluation should regard such orbitals as accidentally degenerate. Although the calculated discrepancy is significantly larger in both of the *ab initio* approaches, they too ultimately rely upon the adequacy of *Koopmans*' theorem.

For this reason, we have also performed an open-shell STO-3G *Hartree-Fock* treatment of *Dewar* benzene (**3**) as well as of its radical cation. We find the total energy of **3** to be $\varepsilon(^1\tilde{A}_1) = -227.763022$ *Hartrees.* The electronic ground state of the radical cation, ($^2\tilde{B}_2$), comes at -227.504043; its first excited state ($^2\tilde{A}_1$) appears at -227.498101.

Band ① in the photoelectron spectrum then corresponds to a transition, $^2\tilde{B}_2 \leftarrow {}^1\tilde{A}_1$, of 7.05 eV. Band ② corresponds to $^2\tilde{A}_1 \leftarrow {}^1\tilde{A}_1$ of 7.21 eV. The predicted values are of course much too small, as was to be expected for this type of treatment within the STO-3G approximation.

The important result is that the sequence of states, $^2\tilde{B}_1$ below $^2\tilde{A}_1$, is identical with that derived by applying *Koopmans'* theorem at the same level of approximation. More quantitatively, the energy gap, $\varepsilon(^2\tilde{A}_1)-\varepsilon(^2\tilde{B}_2) = 0.16$ eV, is not significantly larger than $\varepsilon^{\mathrm{STO\text{-}3G}}(5b_2)-\varepsilon^{\mathrm{STO\text{-}3G}}(8a_1) = 0.08$ eV (Table 3).

We conclude that the removal of an electron from molecular orbitals $5b_2$ and $8a_1$ induces almost equal electron rearrangements in the radical cation as compared with the charge distribution expected for the hypothetical *Koopmans'* process. This, in turn, implies that the orbitals $5b_2$ and $8a_1$ occupy similar regions of space in *Dewar* benzene, a conclusion that is wholly supported by all the analyses of the preceding sections.

Conclusions. – *Dewar* benzene is clearly the most anomalous member of the series of bridged bicyclic dienes **I**(n). And yet, it is now clear, the reasons for its anomalous photoelectron spectrum follow quite logically from those which guided the more regular pattern of its higher homologues. Removal of the last bridging CH_2 group widens the dihedral angle and thus attenuates 'through-space' interaction. The C–C bonds which link the bridgehead carbon atoms to the olefinic ones continue to play an important role in transmitting 'through-bond' interaction. So too, now, do the bridgehead CH bonds. The central C–C bond — abnormally long and weak as it no doubt is — plays a distinctly secondary role in the photoelectron spectrum.

Our assignment of the 'natural order' to the π-bonds of *Dewar* benzene illustrates the difficulties that are involved when only a small gap separates two ionization energies. The consistency of the results obtained by empirical deduction, by several semiempirical calculations, and by an open-shell calculation leaves little room for doubt. Our other two assignments — of the 'inverted order' in the hexamethyl derivative **6** and of the 'natural order' in the hexafluoro **7** — were derived solely by empirical deduction and SPINDO calculation. Nevertheless, since the separation of the first two bands in both compounds is significantly greater than those of the unsubstituted hydrocarbon, we doubt that a more thorough analysis would ever reverse these assignments.

Experimental Part

Bicyclo[2.2.0]hexa-2,4-diene ((**3**, *Dewar* benzene) was obtained by minor modification of the *van Tamelen* procedure [2] [11]. Typically, 750 mg *exo,exo*-5,6-dicarboxybicyclo[2.2.0]hex-2-ene [11], 50 mg *4-t-butylcatechol*, and 1.25 ml triethylamine in 50 ml pyridine/water 10.6:1 was electrolysed at 150 V, 25 ± 3°. Isopentane extraction and concentration was followed by GC. purification through 457 × 0.64 cm 10% *Ucon* Polar LB55OX on Chromosorb W at a column temperature of 45°. In this way, 17–23% of product contaminated by less than 3% benzene was routinely obtained. – ^{1}H-NMR. (CCl_4): δ 6.53 (*t*, 3.98 ± 0.03, $J = 0.6$ Hz) and 3.88 (*quint.* 2.02 ± 0.03, $J = 0.6$ Hz) ppm [lit. [2] (pyridine): 6.55 (*t*, 4, $J = 0.7$ Hz) and 3.84 (*quint.*, 2, $J = 0.7$ Hz) ppm] *Caution.* As noted by others [4e] sealed vials of this hydrocarbon occasionally detonate for unknown reasons.

Bicyclo[2.2.0]hex-2-ene (**2**) was prepared from *exo,exo*-2,3-dicarboxylbicyclo[2.2.0]hexane [11], was isolated and was purified in essentially the same way as was **3**, thus providing GC. homogeneous **2** in 32% yield. – ^{1}H-NMR. (CCl_4): δ 6.33 (1.90 ± 0.03); 3.30 (1.93 ± 0.02) and 2.5–1.5 (4.18 ± 0.03) ppm [lit. [11] (CCl_4): δ 6.15, 3.17 and 2.4–1.3 ppm].

Bicyclo[2.2.0]hexane (**1**) was obtained from an isopentane solution of **2** by adding 50 mg Pd/C at −30° and hydrogenating at 4 atm as the solution equilibrated to RT. Purification as above provided a 21% yield of material (from the dicarboxylic acid precursor), characterized by its uniquely complex ^{1}H-NMR. spectrum [10].

Hexafluoro Dewar *benzene* (**7**) has been prepared by UV.-irradiation of hexafluorobenzene in the gas-phase [14]. The sample was purified by GC. Its IR. and ^{19}F-NMR. spectra were in agreement with published data [14].

Note. This paper was submitted in December 1975 to Z. phys. Chem. (N.F.). Due to an unfortunate set of circumstances the manuscript was lost, a fact of which we were notified only nine months later. Although the part concerned with hexafluoro *Dewar* benzene (**7**) duplicates the results obtained in the meantime by *Delwiche & Preat* [16], we have preferred to leave it as it originally stood, to preserve the continuity of the presentation.

We wish to thank Drs. *C. R. Brundle, M. B. Robin* and *N. A. Kuebler* who generously put the photoelectron spectra of the compounds **4**, **5**, and **6** at our disposal.

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