Physical and Inorganic Chemistry

Electron Spin Resonance Studies of the Radical Anions of [2.2]Paracyclophane and Related Compounds

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Abstract: Esr spectra of the radical anion of [2.2]paracyclophane in a variety of solvents have been analyzed. Taken in 1,2-dimethoxyethane solution, the spectra are characteristic of an unassociated species (symmetry D_{2h}), whereas in tetrahydrofuran they give evidence of ion-pair formation between the radical anion and an alkali metal cation (symmetry C_{2v}). Coupling constants have been unequivocally assigned to sets of equivalent protons by means of 4,12-dideuterium substitution. Bromination of [2.2]paracyclophane, an intermediate step in the synthesis of the ring-deuterated derivative, yielded 4,12-dibromo[2.2]paracyclophane, as well as the 4,13 isomer and higher brominated products. The radical anion of [3.3]paracyclophane has also been studied and its esr spectrum discussed in terms of possible conformations. Investigation of this radical anion, together with that of [4.4]para-cyclophane, led to the conclusion that the number n of methylene groups separating the two benzene rings in [n.n]paracyclophanes must be larger than three to prevent the unpaired electron from delocalizing over both moieties. In the case of the open-chain compounds, on the other hand, the corresponding requirement is $n > 1$, as is shown by the esr study of the radical anions of diphenylmethane, bibenzyl, and bis(4-methylbenzyl). These results suggest that a different mechanism is responsible for the electron transfer between the two benzene rings in the radical anions of bridged and open-chain compounds. Finally, a simple MO model has been considered which accounts for the relative energy and the symmetry of the singly occupied orbital in the radical anions investigated.

Since [2.2]paracyclophane was first synthesized by Cram and Steinberg,[2] its physicochemical properties and electronic structure have been the subject of a number of papers.[3-5] Two of these papers have dealt with the esr spectrum of its radical anion. The first study was that of Weissmann[4] who reduced [2.2]paracyclophane by potassium in 1,2-dimethoxyethane. He observed "a poorly resolved spectrum of at least nine components" but reported no coupling constants. The subsequent paper by Ishitani and Nagakura[5] included the discussion of an esr spectrum obtained by reducing [2.2]paracyclophane with Na|K alloy in tetrahydrofuran. This spectrum had been analyzed in terms of 41 components spaced by 0.63 G. Two coupling constants,

2.52 and 0.63 G, each for eight equivalent protons, were estimated therefrom. Using arguments based on a charge-transfer model, Ishitani and Nagakura assigned the smaller coupling constant to the ring protons and the larger one to the protons in the methylene groups.

We have investigated the esr spectra of the radical anions produced from [2.2]paracyclophane (I) by potassium reduction in a number of solvents. Owing to the high resolution of the spectra, combined with computer simulation, we have been able to carry out a detailed analysis of the hyperfine structure. Moreover, comparison with the spectra obtained under the same conditions from 4,12-dideuterio[2.2]paracyclophane (II) led to unequivocal assignment of the coupling constants to sets of equivalent protons.

Electron transfer between the two benzene rings in paracyclophanes has been of major interest in the esr studies of their radical anions.[4,6] This situation prompted us to investigate the radical anions of some

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(2) D. J. Cram and H. Steinberg, J. Amer. Chem. Soc., 73, 5691 (1951).

(3) For references up to 1963, see B. H. Smith, "Bridged Aromatic Compounds," Academic Press, New York, N. Y., 1964.

(4) S. I. Weissmann, J. Amer. Chem. Soc., 80, 6462 (1958).

(5) A. Ishitani and S. Nagakura, Mol. Phys., 12, 1 (1967).

(6) H. M. McConnell, J. Chem.Phys., 35, 508 (1961).

Table I. Proton Chemical Shifts and Spin-Spin Couplings of 4,12- and 4,13-Dibromo[2.2]paracyclophanes[14]

	4,12-Dibromo deriv	4,13-Dibromo deriv
Chemical shifts (ppm)	H-8 and -16, 6.41	H-7 and -16, 6.45
	H-5 and -13, 6.50	H-5 and -12, 6.58
	H-7 and -15, 7.15	H-8 and -15, 7.18
Spin-spin couplings (Hz)	$J_{7,8} = J_{15,16} = 8$	$J_{7,8} = J_{15,16} = 8$
	$J_{5,7} = J_{13,15} = 2$	$J_{5,7} = J_{12,16} = 2$
	$J_{5,8} = J_{13,16} \leqslant 0.5$	$J_{5,8} = J_{12,15} \leqslant 0.5$
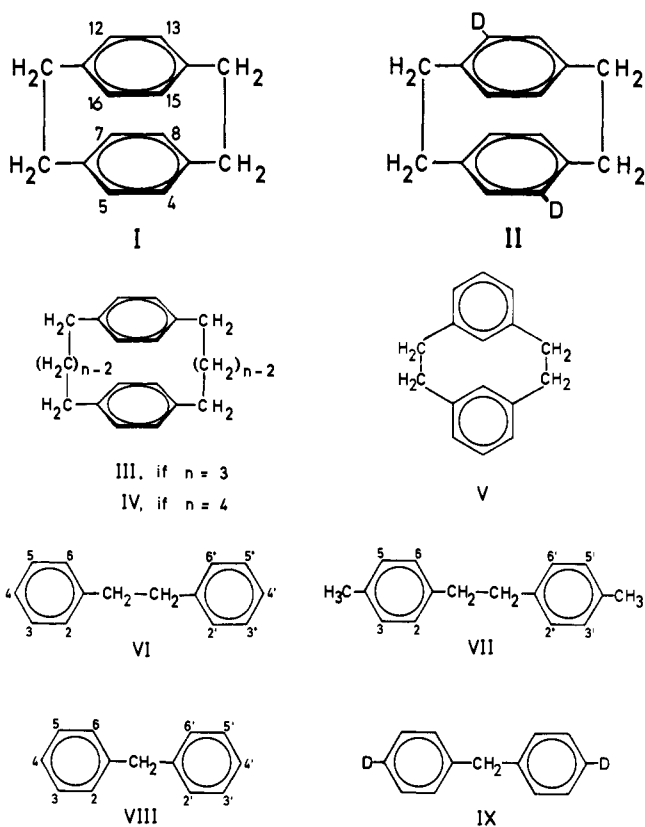
related bridged and open-chain compounds (III–IX) also containing two benzene rings linked by methylene groups. Of these, to our knowledge only the radical anions of [4.4]paracyclophane (IV)[4] and bibenzyl (VI)[7] have been studied so far. Whereas for the radical anion of IV our results agree with those published previously, there is a considerable disagreement in the case of the radical anion of VI.

Experimental Section[8]

Source of Compounds. [2.2]Paracyclophane (I), purchased from Aldrich Chemical Co. Inc., Milwaukee, Wis., was purified by sublimation *in vacuo*, mp 287–289°.

[3.3]- and [4.4]paracyclophanes (III and IV, respectively) were kindly provided by Professor D. J. Cram, U.C.L.A.; mp 104 (III) and 106° (IV).

[2.2]Metacyclophane (V) was a generous gift of Professor W. Jenny, CIBA AG, Basel, Switzerland; mp 135°.

Bibenzyl (VI) and diphenylmethane (VIII), purchased from Fluka AG, Buchs, Switzerland, were both purified by sublimation *in vacuo*; mp 52 (VI) and 25° (VIII).

(7) V. V. Voevodskii, S. P. Solodovnikov, and V. M. Chibrikin, *Dokl. Akad. Nauk SSSR*, **129**, 1082 (1959); S. P. Solodovnikov, *Zh. Strukt. Khim.*, **2**, 282 (1961).

(8) All melting points listed are uncorrected.

Bis(4-methylbenzyl) (VII) was synthesized from 4-methylbenzyl bromide by a standard Grignard coupling reaction.[9] Chromatography on alumina and recrystallization from petroleum ether resulted in crystals having the melting point reported in the literature:[10] 85–86°.

4,4′-Dideuteriodiphenylmethane (IX) was produced from the 4,4′-dibromo derivative (mp 62–64°)[11] which had been obtained by bromination of VIII. The conversion of the dibromo into the dideuterio compound (IX) proceeded *via* the dilithium intermediate following a well-known method.[12] The isotopic purity was 98%, according to mass spectroscopy.

4,12-Dideuterio[2.2]paracyclophane (II) was prepared in an analogous way from the corresponding dibromo derivative. The deuterated product consisted of 85% of 4,12-dideuterio[2.2]paracyclophane, as shown by mass spectroscopy. The 4-deuterio derivative was the next major component, constituting another 14% of the product.

The synthetic method followed for 4,12-dibromo[2.2]paracyclophane is briefly described below.[13]

Bromination of [2.2]Paracyclophane. Bromine (0.726 g, 4.54 mmole) in 15 ml of dry methylene chloride was added to 0.201 g (0.96 mmole) of [2.2]paracyclophane (I) in the same amount of solvent, containing 9 mg of iron filings. The reaction mixture was refluxed for 1 hr and subsequently stirred at room temperature for 2 days. Filtration from insoluble material and evaporation of the solvent yielded the crude product which was purified by chromatography on neutral alumina (Woelm, Activity I) and recrystallization from benzene–methanol and benzene–petroleum ether mixtures. Three fractions, A, B, and C, consisting of yellowish crystals, and melting at 238–240, 251–253, and 261–263°, respectively, were isolated and identified by various analytical means.

Proton resonance spectra showed fraction B to be almost exclusively 4,12-dibromo[2.2]paracyclophane, while fraction A consisted of the isomeric 4,12- and 4,13-dibromo derivatives in an approximate 2:1 ratio. The characteristic resonance data of the ring protons in the two isomers can be summarized as shown in Table I.[14]

Fraction C proved to be a mixture of higher brominated derivatives of [2.2]paracyclophane. Its proton resonance spectrum has not been analyzed in detail.

For the synthesis of 4,12-dideuterio[2.2]paracyclophane (see above), only the fraction B was used.

Preparation of Radical Anions. Potassium as reducing agent and tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) as solvent were used for the preparation of the radical anions from the compounds I–IX. In a few cases a small percentage of hexa-

(9) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, pp 131–132.

(10) P. Carre, *Compt. Rend.*, **148**, 1108 (1909).

(11) N. E. Goldthwaite, *Amer. Chem. J.*, **30**, 447 (1903).

(12) See, *e.g.*, J. Heinzer, "Diplomarbeit," Eidg. Technische Hochschule, 1964.

(13) Shortly before dispatch of this paper, we came across a preliminary communication on electrophilic substitution of [2.2]paracyclophane: H. J. Reich and D. J. Cram, *J. Amer. Chem. Soc.*, **90**, 1365 (1968). The bromination reagents and the methods used to identify the products resemble those described in our paper, but no experimental details were given. The authors also found that the main dibromo product was the 4,12 derivative which has been denoted by them as pseudo-*para*.

(14) Solvent, deuteriochloroform; temperature, +23°; frequency, 100 MHz; chemical shifts, relative to tetramethylsilane (δ values). The experimental error in the chemical shifts and spin-spin couplings are 0.02 ppm and 0.5 Hz, respectively.
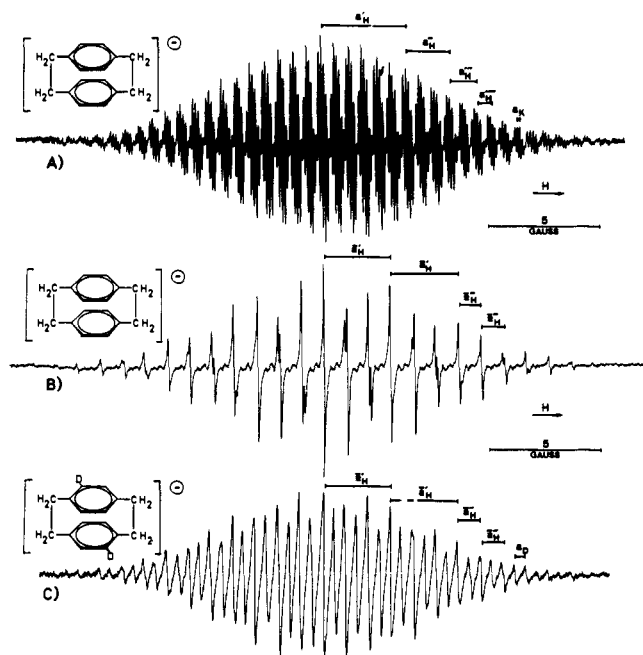
Figure 1. Esr spectra of the radical anions of [2.2]paracyclophane (A and B) and its 4,12-dideuterio derivative (C, containing 14% of 4-deuterio[2.2]paracyclophane); solvent tetrahydrofuran (A) or 1,2-dimethoxyethane with 2-3% hexamethylphosphoramide (B and C), temperature $-85°$ (A) or $-95°$ (B and C).
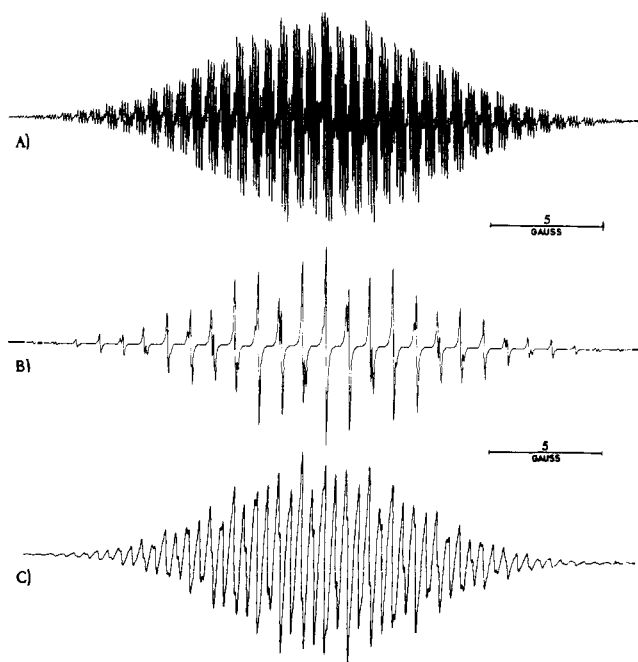

Figure 2. Computer-simulated esr spectra of the radical anions of [2.2]paracyclophane (A and B) and its 4,12-dideuterio derivative (C). Coupling parameters used (in gauss): (A) $a_H' = 3.78$, $a_H'' = 1.96$, $a_H''' = 1.27$, and $a_H'''' = 0.68$, each for four equivalent protons, and $a_K = 0.120$ for one ^{39}K nucleus; (B) $\bar{a}_H' = 2.97$ and $\bar{a}_H'' = 1.03$, each for eight equivalent protons; (C) 86%, $\bar{a}_H' = 2.97$ and $\bar{a}_H'' = 1.03$, for six and eight equivalent protons, respectively, and $a_D = 0.46$ for two equivalent deuterons; 14%, $\bar{a}_H' = 2.97$ and $\bar{a}_H'' = 1.03$, for seven and eight equivalent protons, respectively, and $a_D = 0.46$ for one deuteron.

methylphosphoramide (HMPA)was added to the DME solutions.

Both alkali metal reduction and recording of the spectra were carried out at temperatures below $-70°$. [4.4]Paracyclophane (IV), bibenzyl (VI), and bis(4-methylbenzyl) (VII) reacted less readily with potassium than [2.2]- and [3.3]paracyclophanes (I and III, respectively) and diphenylmethane (VIII). While the radical anions of all these compounds were stable for hours at low temperatures, the radical anion of [2.2]metacyclophane (V) underwent chemical conversion very rapidly even at -80 to $-100°$ (cf. Analysis of the Esr Spectra).

Instrumental. The proton resonance spectra were taken on a Varian A-100. The mass spectrometer used was Hitachi-Perkin-Elmer RMU-6D. The esr spectra were recorded on a Varian V-4502 equipped with a 9-in. magnet. The coupling constants were calibrated by simultaneous display of the Fremy-salt signals whose separation has been given the value of 13.0 G.

The simulated esr spectra, which assume Lorentzian line shape and appropriate line widths, were generated by a computer program ESRSIMO3 developed by Dr. J. Heinzer of this laboratory. The computer was a CDC-1604 associated with a CALCOMP plotter 565.

Analysis of the Esr Spectra

Radical Anion (I⁻) of [2.2]Paracyclophane. Figure 1A shows the esr spectrum of I⁻ obtained in tetrahydrofuran (THF) solution at $-85°$. Although it roughly corresponds to the spectrum observed by Ishitani and Nagakura,[5] it exhibits two features unnoted by these authors. Firstly, owing to considerably higher resolution, each of the previously observed 41 components splits into four to six narrow lines; secondly, with higher sensitivity, four additional components—or rather groups of lines—are identified on each end of the spectrum. That means that the over-all number of resolved lines has increased from 41 to 49 times (4...6) ≈ 200...300.

The pattern of the spectrum with 49 groups of lines is due to the proton coupling constants which are rough multiples of the spacing between the groups. The splitting within each group, on the other hand, results

from the coupling with a ^{39}K nucleus and from the inexactness of the above-mentioned spacing relations.[15]

The computer-simulated spectrum agrees satisfactorily with the experimental one, if the values (in gauss)

$$a_H' = 3.78 \pm 0.04 \qquad a_H'' = 1.96 \pm 0.03$$
$$a_H''' = 1.27 \pm 0.02 \qquad a_H'''' = 0.68 \pm 0.01$$

and

$$a_K = 0.120 \pm 0.005$$

are adopted for four sets of four equivalent protons and one ^{39}K nucleus, respectively.[15] This can be seen by comparing Figure 1A with 2A in which the simulated spectrum is reproduced.

Use of 1,2-dimethoxyethane (DME) as a solvent leads to a largely simplified spectrum whose hyperfine structure is consistent with two sets of eight equivalent protons. The quality of the spectrum can be improved by adding small amounts (2-3%) of hexamethylphosphoramide (HMPA) to the DME solution. Figure 1B shows a spectrum taken at $-95°$ in such a DME-HMPA mixture. The analysis of the hyperfine structure readily yields the two coupling constants (in gauss)

$$\bar{a}_H' = 2.97 \pm 0.02 \qquad \bar{a}_H'' = 1.03 \pm 0.01$$

for the two sets of eight equivalent protons in I⁻. A computer-simulated spectrum based on these values is

(15) An identical spectrum is obtained, if, in the preparation of I⁻, potassium is replaced by Na K alloy, the reducing agent used by Ishitani and Nagakura.[5] In particular, the same splitting from the alkali metal nucleus is observed. This fact can be explained by the selectivity of [2.2]paracyclophane in respect to sodium and potassium, the reaction with the latter being highly favored.
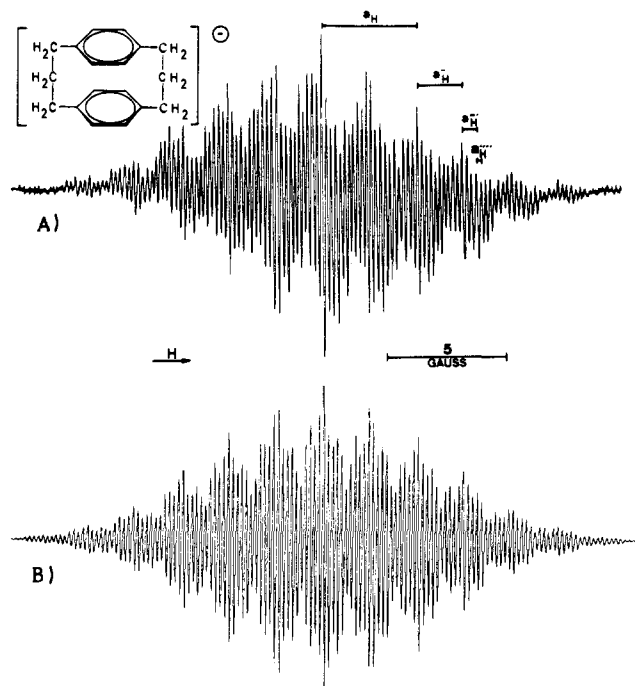
Figure 3. Esr spectra of the radical anion of [3.3]paracyclophane: (A) solvent 1,2-dimethoxyethane with 2–3% hexamethylphosphoramide, temperature $-90°$; (B) computer-simulated spectrum. Coupling parameters used (in gauss): $a_H' = 3.95$, $a_H'' = 1.88$, $a_H''' = 0.575$, and $a_H'''' = 0.192$, each for four equivalent protons.

reproduced in Figure 2B. The smallest observable splitting of 0.12 G clearly results from the difference $3\bar{a}_H'' - \bar{a}_H'$. The satellite lines, which are apparent in the experimental spectrum (Figure 1B) but missing in the simulated one (Figure 2B), certainly arise from the interaction with radical anions containing a ^{13}C nucleus. Although, owing to the high symmetry of the radical anions, the satellites are relatively intense, overlapping prevents a reliable analysis.

Radical Anion (II⁻) of 4,12-Dideuterio[2.2]paracyclophane. Figure 1C shows the spectrum of II⁻ taken in DME–HMPA, i.e., under the same conditions as that presented in Figure 1B for I⁻. The hyperfine structure of II⁻ can be satisfactorily analyzed in terms of the coupling constants $\bar{a}_H' = 2.97$ and $\bar{a}_H'' = 1.03$ G for six and eight equivalent protons, respectively, and $a_D = 0.1535 \cdot \bar{a}_H' = 0.46$ G for two equivalent deuterons. The spectrum simulated by means of these values is reproduced in Figure 2C. It allows also for the radical anion of the mono deuterated [2.2]paracyclophane present as isotopic impurity.

Radical Anion (III⁻) of [3.3]Paracyclophane. The esr spectrum of III⁻ in DME is very sensitive to temperature. Its intensity, which is considerable at -80 to $-95°$, diminishes on warming. The signals vanish at $-50°$ and do not reappear upon further increases in temperature up to $+60°$. This behavior, however, is not due to radical decay, since mere recooling to $-80°$ renews the original intense spectrum. Addition of 2–3% HMPA to DME improves the resolution greatly. Figure 3A shows an esr spectrum obtained at $-90°$ in this solvent mixture. It compares favorably with the simulated spectrum reproduced in Figure 3B and based on the following coupling constants for four sets of four equivalent protons (in gauss).
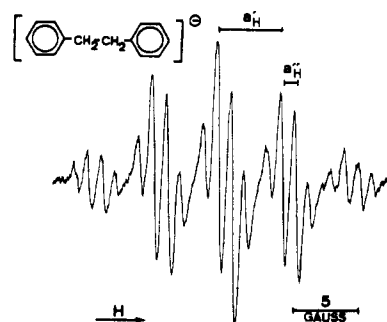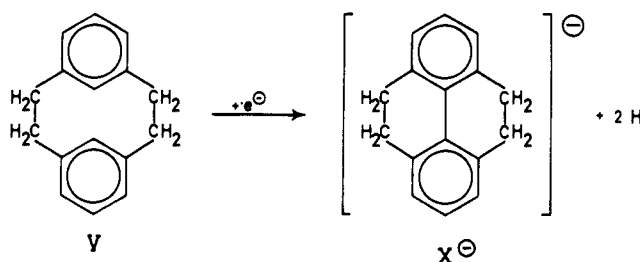

Figure 4. Esr spectrum of the radical anion of bibenzyl: solvent 1,2-dimethoxyethane, temperature $-90°$.

$$a_H' = 3.95 \pm 0.04 \qquad a_H'' = 1.88 \pm 0.02$$

$$a_H''' = 0.575 \pm 0.01 \qquad a_H'''' = 0.192 \pm 0.005$$

Radical Anion (IV⁻) of [4.4]Paracyclophane. The available amount of [4.4]paracyclophane (IV) was not sufficient to obtain an intense esr spectrum, considering the difficult reducibility of the compound. Nevertheless, by the use of large modulation and high signal level, five broad components, due to four equivalent protons, could be observed in DME at low temperatures. The proton coupling constant $a_H = 5.35 \pm 0.10$ G is, within the limits of the experimental error, equal to that reported by Weissmann.[4] The width of the components suggests that the remaining splittings are less than 0.3 G.

Radical Anion (V⁻) of [2.2]Metacyclophane. The esr spectra obtained on reduction of [2.2]metacyclophane (V) in DME were identical with that of the radical anion of 4,5,9,10-tetrahydropyrene (X).[16] Numerous attempts to generate the esr spectrum of the primary reduction product, i.e., the radical anion V⁻, have failed so far, despite extreme precautions. The uptake of an extra electron by V must therefore have been followed by immediate elimination (within 1 min or less) of two hydrogens to yield X⁻.

Radical Anion VI⁻ of Bibenzyl. Figure 4 shows the esr spectrum of VI⁻ in DME. The hyperfine pattern of five groups of four lines is due to two sets of four and three equivalent (or nearly equivalent) protons having the coupling constants $a_H' = 4.83 \pm 0.06$ and $a_H'' = 1.02 \pm 0.02$ G, respectively. This spectrum differs completely from that published previously.[7]

Radical Anion (VII⁻) of Bis(4-methylbenzyl). The esr spectrum of VII⁻ in DME exhibits five broad components. The coupling constants of the four equivalent (or nearly equivalent) protons responsible for these com-

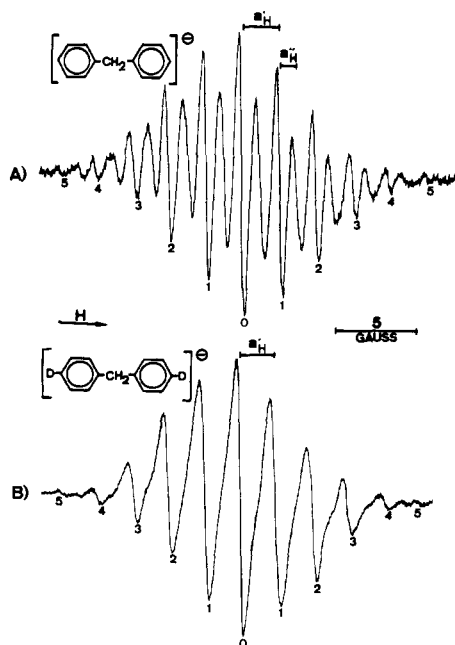(16) M. Iwaizumi and T. Isobe, *Bull. Chem. Soc. Japan*, **38**, 1547 (1965).

Figure 5. Esr spectra of the radical anions of diphenylmethane (A) and its 4,4'-dideuterio derivative (B); solvent 1,2-dimethoxyethane, temperature −90°.

Figure 6. Position of the gegenion relative to the radical anion of [2.2]paracyclophane.

ponents is $a_H = 5.20 \pm 0.08$ G. The remaining protons apparently give rise to splitting of less than 0.2 G, as can be deduced from the line width.

Radical Anion (VIII⁻) of Diphenylmethane. The esr spectrum of VIII⁻ in DME is shown in Figure 5A. The 11 equidistant lines marked by numbers stem from a set of ten equivalent (or nearly equivalent) protons with a coupling constant $a_H' = 2.23 \pm 0.04$ G. A further splitting, $a_H'' = 0.89 \pm 0.03$ G, arises from the hyperfine interaction with a pair of equivalent protons.

Radical Anion (IX⁻) of 4,4'-Dideuteriodiphenylmethane. The spectrum of IX⁻ (Figure 5B) differs from that of VIII⁻ by the absence of the splitting $a_H'' = 0.89$ G. Although the corresponding splitting $a_D = 0.1535 \cdot a_H''$ = 0.135 G, due to two equivalent deuterons, could not be resolved, its presence is indicated by the width of the 11 hyperfine components of IX⁻, which is highly enhanced relative to that of corresponding lines of VIII⁻.

Interpretation of the Esr Spectra

Radical Anion (I⁻) of [2.2]Paracyclophane. It is evident that the relative complexity of the esr spectrum of I⁻ in tetrahydrofuran (Figure 1A) arises from an association between the radical anion and its gegenion. This is well documented by the appearance of the hyperfine splitting due to the ^{39}K nucleus $(I = {}^3/_2)$ of the gegenion: $a_K = 0.120$ G.

For steric reasons, the gegenion cannot stay at the symmetry center of the radical anion I⁻ and, therefore, any tight association must lead to a reduction of symmetry from D_{2h} to C_{2v} at best. The four coupling constants observed, a_H', a_H'', a_H''', and a_H'''', each for a set of four equivalent protons, are consistent with the symmetry C_{2v} of an ion pair, since the reduction of D_{2h} to this symmetry should result in separating each of the two sets of eight equivalent protons into two sets of four.
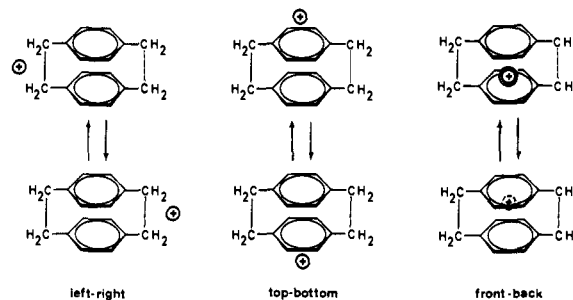
The position of the gegenion K^+ relative to the radical anion I⁻ cannot, however, be determined from the esr spectrum (Figure 1A), as there are three nonequivalent ion pairs having the required symmetry C_{2v}. Each of the three ion pairs is converted into its mirror image by the transfer of the gegenion to the opposite side of the radical anion (Figure 6).

Fortunately, it is possible to interpret the esr hyperfine pattern of I⁻ in different solvents without knowing exactly which of the three nonequivalent ion pairs actually occurs. The hyperfine pattern depends on the interconversion rate between a given ion pair and its mirror image, the critical rate being $\gamma_E \Delta a_H$, where $\gamma_E = 2.802$ MHz G^{-1} denotes the gyromagnetic ratio of the electron, and Δa_H is the difference between the coupling constants exchanged by this interconversion. It is clear that, when an ion pair passes over into its mirror image, two sets of four ring and four methylene protons interchange their coupling constants with two corresponding sets of four ring and four methylene protons, and that the protons affected are those which have been made nonequivalent by the association with the gegenion.

In tetrahydrofuran (THF), the interconversion rate is slower than $\gamma_E \Delta a_H$, so that the esr spectrum of an ion pair or its mirror image is observed, both giving rise to identical hyperfine structures (Figure 1A). As might be anticipated, addition of 1,2-dimethoxyethane (DME) with its higher solvating power weakens the pairing tendency, and the interconversion rate is enhanced. Figure 7 shows the central part of an esr spectrum taken in a
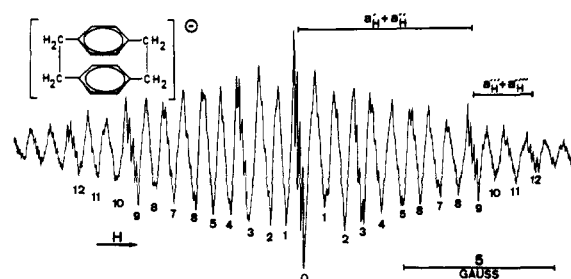

Figure 7. Esr spectrum of the radical anion of [2.2]paracyclophane (central part) showing anomalous line broadening; solvent, 1,2-dimethoxyethane–tetrahydrofuran (ratio 2:1), temperature −80°.

THF–DME 1:2 mixture at −80°. This spectrum still exhibits the over-all hyperfine pattern seen in pure THF (Figure 1A), since it consists of 49 groups of lines spaced by 0.6–0.7 G. However, the lines are now considerably broadened so that the splitting within the groups is mostly lost. The remarkable feature is the

difference in resolution of the individual groups. It can be seen from Figure 7 that the central group, numbered 0, is best resolved. Relatively good resolution characterizes also the groups 9, and to a lesser degree, 3 and 12. Comparing the spectra in Figures 7 and 1A, one notes that the distances between the groups 0 and 9, on one hand, and between 0 and 3 or 9 and 12, on the other hand, correspond to the sum $a_H' + a_H'' \approx 5.7 \pm 0.1$ and $a_H''' + a_H'''' \approx 1.95 \pm 0.05$ G, respectively.

Similar phenomena have been frequently reported in the last few years,[17] and the theory underlying them is now well understood.[18] It enables us here to draw some conclusions from the anomalous line broadening observed, without recourse to a detailed study of the line width.

The anomalous line broadening occurs because the interconversion rate is now comparable to $\gamma_E \Delta a_H$, this being also the rate at which the two sets of four ring and of four methylene protons interchange their coupling constants with the corresponding two sets. Moreover, the above-mentioned relation between the positions of the resolved groups (Figure 7) and the sums of the coupling constants (Figure 1A) tells us that (1) a_H' is interchanged with a_H'', both having identical signs; (2) the same holds for a_H''' and a_H''''; and (3) the interconversion rate is comparable to $\gamma_E(a_H' - a_H'')$ or $\gamma_E(a_H''' - a_H'''')$, i.e., of the order 10^6–10^7 sec^{-1}.

The conclusions stated under (1) and (2) are fully justified by the esr spectrum taken in a mixture of 1,2-dimethoxyethane and hexamethylphosphoramide (DME–HMPA, Figure 1B). In this medium of a relatively high solvation power, the interconversion rate is larger than 10^7 sec^{-1} and coupling constants a_H' and a_H'', on one hand, and a_H''' and a_H'''', on the other hand, should be averaged. In fact, the hyperfine splittings $\bar{a}_H'$ and $\bar{a}_H''$ measured in DME–HMPA, each for a set of eight equivalent protons, are close to the arithmetic means of those found in THF. The small deviations (ca. 4%) between $^1/_2(a_H' + a_H'') = {}^1/_2(3.78 + 1.96) = 2.87$ and $\bar{a}_H' = 2.97$ G and between $^1/_2(a_H''' + a_H''') = {}^1/_2(1.27 + 0.68) = 0.98$ and $\bar{a}_H'' = 1.03$ G are presumably due to different solvents, rather than to the tiny spin populations carried over to the gegenions in the ion pairs.

The increase of the solvating power of the medium on passing from THF to DME–HMPA thus restores the full symmetry D_{2h} of an unassociated radical anion I$^-$.

The assignment of the two coupling constants $\bar{a}_H'$ and $\bar{a}_H''$ found for I$^-$ in DME–HMPA clearly results from the esr spectrum of the radical anion II$^-$ of 4,12-dideuterio[2.2]paracyclophane in the same medium (Figure 1C). Since a splitting $a_D = 0.1535 \cdot \bar{a}_H' = 0.46$ G for two equivalent deuterons is now observed, the set of eight equivalent protons with the coupling constant $\bar{a}_H'$ being decreased to six, the assignment of $\bar{a}_H' = 2.97$ G to eight equivalent ring protons, and $\bar{a}_H'' = 1.03$ G to eight equivalent methylene protons becomes evident. This assignment is opposed to that proposed by Ishitani and Nagakura[5] who, relying on theoretical arguments,

claimed a larger coupling constant for the methylene rather than for the ring protons.

The proton coupling constants a_H', a_H'', a_H''', and a_H'''' measured for the ion pairs of I$^-$ in THF have, therefore, to be assigned as follows: $a_H' = 3.78$ and $a_H'' = 1.96$ G to two sets of four equivalent ring protons, and $a_H''' = 1.27$ and $a_H'''' = 0.68$ G to two sets of four equivalent methylene protons.

Radical Anion (III$^-$) of [3.3]Paracyclophane. The magnitudes of the four coupling constants a_H', a_H'', a_H''', and a_H'''', each for a set of four equivalent protons in III$^-$, leave no doubt that (similarly to radical anion I$^-$ of [2.2]paracyclophane) the protons of both benzene rings and of all methylene groups adjacent to them (β protons) contribute to the hyperfine structure.[19] By analogy with I$^-$, the coupling constants $a_H' = 3.95$ and $a_H'' = 1.88$ G, whose mean value is 2.92 G, have to be assigned to two sets of four equivalent ring protons. The remaining coupling constants, $a_H''' = 0.575$ and $a_H'''' = 0.192$ G, must thus be due to two sets of four equivalent β protons. The protons in the central methylene groups (γ protons) are expected to give rise to a very small splitting only, which is below the resolution of the esr spectrum.

The experimental conditions under which the four coupling constants a_H', a_H'', a_H''', and a_H'''' were observed (DME–HMPA, $-90°$, Figure 3A) and the insensitivity of the hyperfine structure to relative amounts of HMPA in DME preclude the occurrence of intimate ion pairs like those found for I$^-$ in THF (Figure 1A). The separation of the eight ring protons and the eight β protons, each into two sets of four, cannot therefore be due to an association with the gegenion. Inspection of the molecular model of [3.3]paracyclophane indicates the flexibility of the methylene chains which leads to a large number of conformations. Referring to a proton in a given position, there are four conformations in which the benzene rings are eclipsed and furthest apart. Two conformations have the symmetry C_{2h} and two C_{2v}, those of the same symmetry being mirror images of each other (Figure 8). If the benzene rings are not eclipsed, the symmetry C_{2h} or C_{2v} is reduced to C_2 and C_s, respectively. It can be seen readily from the molecular model that the distance between the benzene rings decreases only slightly if the deviation from the conformations of higher symmetry C_{2h} or C_{2v} remains small, but falls off rapidly when such deviations become considerable. Thus, besides the conformations C_{2h} and C_{2v}, only those conformations C_2 and C_s are probable in which the distortion from the higher symmetry is rather small. It should be noted that also for any preferred distorted conformation C_2 or C_s, a mirror image exists.

The hyperfine structure characterized by four sets of four equivalent protons is consistent with either of the two eclipsed conformations C_{2h} or C_{2v}. In particular, it is reasonable to assign a_H''' to the four equivalent β protons in positions "axial" to the benzene rings, and a_H'''' to the four equivalent β protons in the "equatorial" positions. The assignment of a_H' and a_H'' to individual sets of four equivalent ring protons is less straightfor-

(17) For references see, e.g., F. Gerson, "Hochauflösende ESR-Spektroskopie, dargestellt anhand aromatischer Radikal-Ionen," Verlag Chemie, Weinheim, Germany, 1967, Anhang A.2.3.; English translation, Verlag Chemie, and John Wiley and Sons, Inc., New York, N. Y., in press.
(18) G. K. Fraenkel, J. Phys. Chem. 71, 139 (1967).

(19) The protons denoted α, β, γ, . . . are linked by 1, 2, 3, . . . bonds to the π-electron center. According to this notation, one refers to ring protons as α, whereas β stands for the protons of a methylene or methyl group directly bound to an aromatic ring.
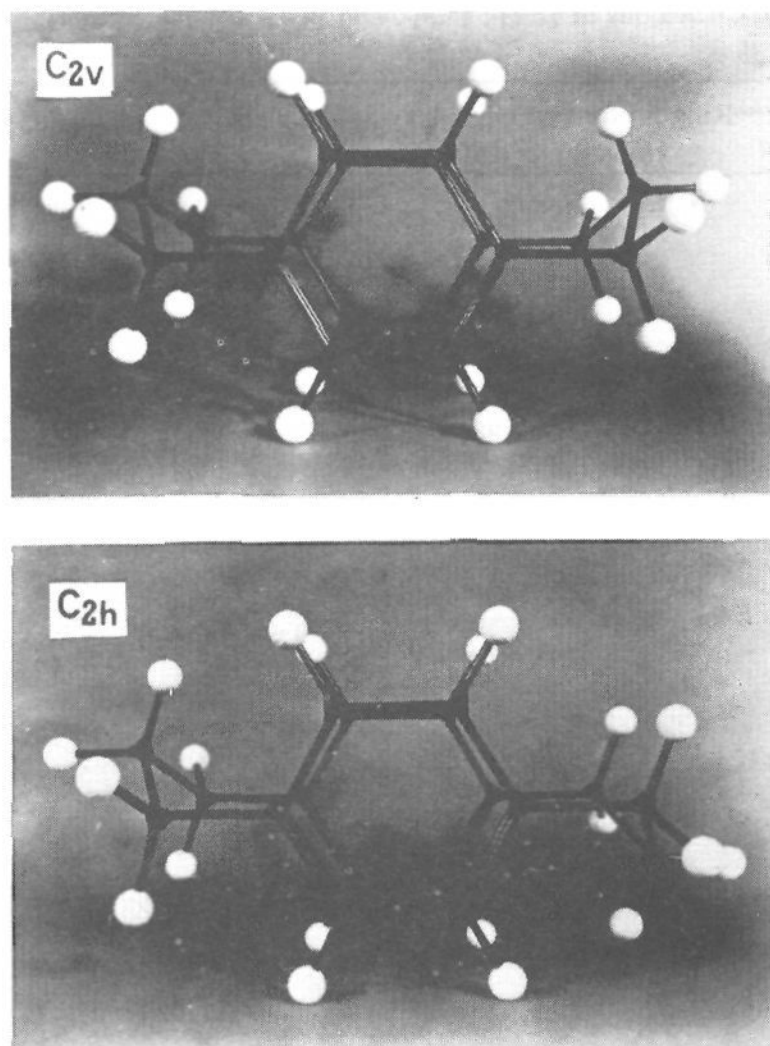
Figure 8. Conformations of the symmetry C_{2v} and C_{2h} of [3.3]-paracyclophane.

ward. Considering the similar environment of these protons in the conformation C_{2h} or C_{2v}, it is hard to rationalize the large differences in the magnitude of their coupling constants. However, a small deviation from the symmetry C_{2h} or C_{2v} yielding the conformations C_2 or C_s suffices to make the environment of four of the ring protons greatly different from that of the four remaining ones.

The low-temperature esr spectrum must arise from the one preferred conformation and its mirror image. The spectral behavior on warming (cf. Analysis) is not yet fully understood. It may be caused by enhanced rate of interconformational conversion and/or by population of an increased number of conformations whose esr spectra are superimposed and smeared.

Radical Anion (IV⁻) of [4.4]Paracyclophane. The coupling constant $a_H = 5.35$ G obtained for four equivalent protons in IV⁻ is almost as large as $2\bar{a}_H' = 5.94$ G, i.e., double the magnitude of the coupling constant of eight equivalent ring protons in the radical anion I⁻ of [2.2]paracyclophane, or as large as $a_H' + a_H'' \approx 5.83$ G, i.e., the sum of the coupling constants of the two sets of four equivalent ring protons in the radical anion III⁻ of [3.3]paracyclophane.

In contrast to I⁻ and III⁻, the hyperfine interaction in IV⁻ is therefore restricted to one moiety of the radical anion, and a_H must be assigned to the four equivalent protons of one benzene ring. This conclusion is substantiated by the comparison of the esr spectrum of IV⁻ with that of the radical anion XI⁻ of diethylbenzene.[20]

The esr spectrum of XI⁻ also consists of five com-

(20) J. R. Bolton, A. Carrington, A. Forman, and L. E. Orgel, Mol. Phys., **5**, 43 (1962).

XI
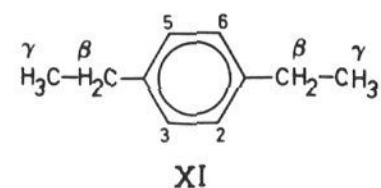
ponents separated by 5.29 G, the coupling constant of four equivalent ring protons, with no resolved splittings from the alkyl β and γ protons.[20]

Radical Anions (VI⁻ and VII⁻) of Bibenzyl and Bis(4-methylbenzyl). The esr spectra of VI⁻ (Figure 4) and VII⁻ closely resemble those of the radical anions XII⁻ and XIII⁻, respectively, derived from the correspondingly substituted alkylbenzenes, ethylbenzene (XII), and 1-ethyl-4-methylbenzene (XIII).[20,21]

XII   XIII
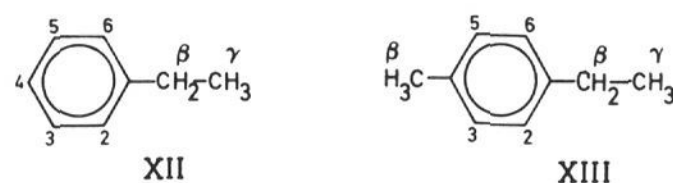
It is therefore reasonable to assume that in VI⁻ and VII⁻ the protons of only one moiety of the radical anion contribute to the hyperfine structure. Moreover, the proton coupling constants for VI⁻ and VII⁻ can be correlated with those for XII⁻ and XIII⁻. Thus in the case of the radical anion VI⁻ of bibenzyl the coupling constants, $a_H' = 4.87$ and $a_H'' = 1.02$ G, of four and three equivalent (or nearly equivalent) protons, respectively, compare favorably with the corresponding values 5.06 and 0.92 G reported for XII⁻.[20] Similarly, the coupling constant $a_H = 5.20$ G of four equivalent (or nearly equivalent) protons in VII⁻ does not differ appreciably from the splitting of 5.34 G observed for the four ring protons in XIII⁻.[21]

By analogy of VI⁻ with XII⁻, a_H' must be assigned to the two pairs of equivalent protons in the 2,6 and 3,5 positions of one benzene ring, whereas a_H'' may be identified with the splitting due to the odd proton in the 4 position of this ring, and to the two methylene β protons. Likewise, the analogy of VII⁻ with XIII⁻ leads to the assignment of a_H to the two pairs of equivalent protons in the 2,6 and 3,5 positions of one benzene ring.[22]

Radical Anion (VIII⁻) of Diphenylmethane. The observation of the splittings $a_H' = 2.23$ and $a_H'' = 0.89$ G, the first holding for ten, and the latter for two equivalent (or nearly equivalent) protons in VIII⁻ (Figure 5A), proves unequivocally that the hyperfine interaction occurs with both moieties of the radical anion. The assignment of a_H'' to the pair of equivalent ring protons in the 4,4' positions results from the comparison of the esr spectrum of VIII⁻ with that of the radical anion IX⁻ of its dideuterated derivative (Figure 5B). The larger coupling constant a_H' must, therefore, be due to the remaining protons, i.e., to the two sets of four equivalent ring protons in positions 2, 6, 2', 6' and 3, 5, 3', 5', as well as to the pair of methylene protons.

(21) E. de Boer and J. P. Colpa, J. Phys. Chem., **71**, 21 (1967).
(22) In the esr spectrum of XII⁻, too, the small splittings from the γ protons could not be resolved.[20] As for XIII⁻, the splittings from the β and γ protons were partially resolved, but not analyzed, because of their complicated hyperfine structure.[21]

Table II. Summary of Proton Coupling Constants (in Gauss) for the Radical Anions of [2.2]-, [3.3]-, and [4.4]Paracyclophanes, and of Diphenylmethane, Bibenzyl, and Bis(4-methylbenzyl)[a]

Group	Radical anion of	Ring protons ortho and meta	Ring protons para	Alkyl protons
A	[2.2]paracyclophane (structure)	2.97 (eight)	...	1.03 (eight)
	[3.3]paracyclophane (structure)	{ 3.95 (four) } { 1.88 (four) } Mean value[b] 2.92 (eight)	...	{ 0.575 (four) } { 0.192 (four) } Mean value[b] 0.384 (eight)
	diphenylmethane (structure)	2.23 (eight)	0.89 (two)	2.23 (two)
B	[4.4]paracyclophane (structure)	5.35 (four)	...	≤0.3
	bibenzyl (structure)	4.83 (four)	1.02 (one)	1.02 (two)
	bis(4-methylbenzyl) (structure)	5.20 (four)	...	≤0.2

[a] Numbers of protons responsible for the coupling constants are given in parentheses. [b] Calculated, not observed.
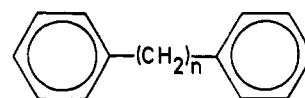
Discussion

The esr results are summarized in Table II in which the radical anions have been arranged in two classes, A and B. The reason for such an arrangement is obvious: class A consists of radical anions in which both moieties contribute to the hyperfine structure, whereas in the radical anions of class B this structure is restricted to one moiety only.

The requirements for a radical anion to enter class A or B are seen to be different for bridged and open-chain species. In the case of [n.n]paracyclophanes, the radical anions of the [2.2] and [3.3] compounds belong to class A, leaving the [4.4] analog in class B. This means that in such radical anions, chains of more than three methylene groups are required to prevent the unpaired electron from delocalizing over both benzene rings. As for the open-chain species, only the radical anion of diphenylmethane, whose benzene rings are linked by but one methylene group, is a member of class A. The radical anions of bibenzyl and bis(4-methylbenzyl), on the other hand, must be included in class B. Thus, in the radical anions of open-chain compounds, two methylene groups suffice to localize the unpaired electron on one benzene ring.[23]

The esr spectra of the radical anions of classes A and B have been denoted by McConnell[6] as fast- and slow-

transfer ones, respectively. This author discussed the mechanism for electron transfer between the two benzene rings in the radical anions of open-chain type. Relying on the inaccurate esr results then available,[7] he considered the same mechanism to be also effective in the radical anions of [n.n']paracyclophanes.
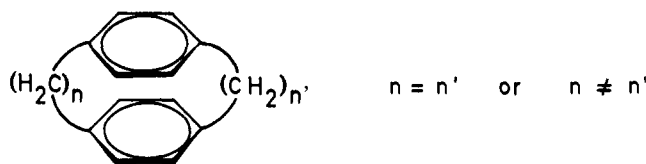
Our results suggest, however, that different mechanisms are responsible for the intramolecular electron transfer in the radical anions of bridged and open-chain compounds, since a higher number of methylene groups is required for the former than for the latter, in order to yield the slow- instead of the fast-transfer spectra. It is tempting to assume that in the radical anions of the open-chain compounds, the electron transfer can be effected solely via the n methylene groups and, as a consequence, it is hampered when $n > 1$. In contrast to this, a direct passage in the direction perpendicular to the two

(23) Analogous conclusion can be drawn from the esr results for the radical anions of bis(4-nitrophenyl)methane and bis(4-nitrobenzyl); cf. J. E. Harriman and A. H. Maki, J. Chem. Phys., **39**, 778 (1963).
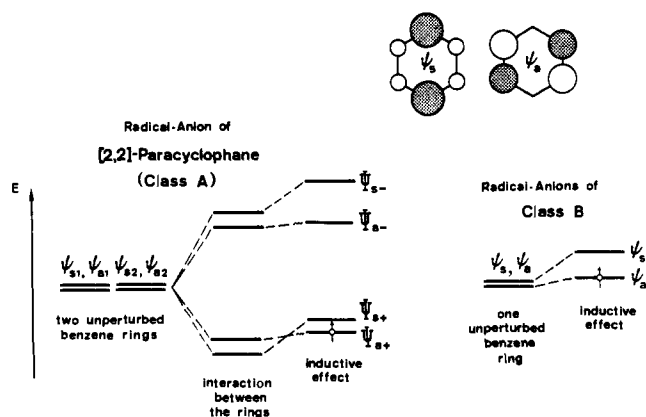
Figure 9. Energy schemes of the lowest antibonding orbitals in [2.2]paracyclophane (class A) and in open-chain compounds with negligible interaction between the benzene rings (class B). Occupancy in the corresponding radical anions. In the schematic representation of the benzene-type MO's and ψ_s and ψ_a, shadowed and empty circles refer to different signs of the LCAO coefficients; the radii of the circles are proportional to their absolute magnitudes.

benzene rings would be favored in the radical anions of [$n.n'$]paracyclophane, when $n, n' \leqslant 3$.

The radical anions of class A and B differ not only in their esr spectra, but also in the ease of formation from the corresponding neutral compounds. As already mentioned in the Experimental Section, [2.2]- and [3.3]-paracyclophanes and diphenylmethane, i.e., the compounds giving rise to the radical anions of class A, could be reduced more readily than [4.4]paracyclophane, bibenzyl, and bis(4-methylbenzyl) from which the radical anions of class B are produced. It is also noteworthy that the radical anions of class B, but not those of class A, are quenched by traces of benzene added to their respective solutions. The electron affinities of [2.2]- and [3.3]paracyclophanes and of diphenylmethane are, therefore, substantially higher than those of [4.4]para-cyclophane, bibenzyl, and bis(4-methylbenzyl). In other words, the lowest antibonding orbital, which takes up the extra electron on passing from the neutral compound to its radical anion, is definitely more stable for the class A systems than for those of class B. This must be due to the stabilizing influence of the interaction between the π-electron systems of the two benzene rings, such an interaction being, of course, effective only in the class A systems.

Figure 9 shows an energy-level diagram for the lowest antibonding orbitals of [2.2]paracyclophane. This diagram is partly based on the calculations by Ishitani and Nagakura.[5] One starts with the two pairs of degenerate antibonding benzene-type MO's, ψ_{s1}–ψ_{a1} and ψ_{s2}–ψ_{a2}, for the rings 1 and 2, respectively, the ψ_s's being symmetric and the ψ_a's antisymmetric relative to a plane passing through the two opposite centers and perpendicular to the benzene ring (cf. Figure 9). The following

four nondegenerate orbitals are obtained therefrom, by the interaction between the π-electron systems of the two rings

$$\Psi_{s+} = N_{s+}(\psi_{s1} + \psi_{s2}) \qquad \Psi_{s-} = N_{s-}(\psi_{s1} - \psi_{s2})$$

$$\Psi_{a+} = N_{a+}(\psi_{a1} + \psi_{a2}) \qquad \Psi_{a-} = N_{a-}(\psi_{a1} - \psi_{a2});$$

where N_{s+}, N_{s-}, N_{a+}, and N_{a-} stand for the normalizing factors. The orbitals Ψ_{s+} and Ψ_{a+} are here symmetric, whereas Ψ_{s-} and Ψ_{a-} are antisymmetric with respect to the mirror plane passing through the inversion center of [2.2]paracyclophane and parallel to the two benzene rings.

As can be seen from Figure 9, the "plus" combinations, Ψ_{s+} and Ψ_{a+}, come out to be more stable than the "minus" ones, Ψ_{s-} and Ψ_{a-}. Moreover, if the inductive effect of the methylene groups is not accounted for, Ψ_{s+} has a slightly lower energy than Ψ_{a+}. Since Ishitani and Nagakura considered this effect to be a negligible quantity compared to the interaction between the two benzene rings, they identified Ψ_{s+} as the singly occupied orbital in the radical anion of [2.2]paracyclophane. The experimental findings (cf. Table II), however, contradict such a conclusion and prove unequivocally that Ψ_{a+} and not Ψ_{s+} take up the unpaired electron. The inductive effect of the methylene groups must thus reverse the energy sequence of the orbitals Ψ_{s+} and Ψ_{a+}, the former being more strongly destabilized than the latter. It would be difficult to derive analogous energy diagrams for [3.3]paracyclophane and diphenylmethane, since the flexibility of these molecules requires several conformations to be considered. Nevertheless, the experimental data reveal that the singly occupied orbital in the radical anions of the two compounds is also a linear combination of the antisymmetric benzene-type MO's ψ_{a1} and ψ_{a2}; i.e., it is similar to Ψ_{a+} or Ψ_{a-}.

In contrast to the class A systems, those of class B present an energy diagram characteristic of the correspondingly substituted alkylbenzenes. This diagram clearly results from the inductive effect of the methylene groups which destabilizes the symmetric benzene-type MO ψ_s to a higher extent than the antisymmetric MO ψ_a, the latter becoming thus the singly occupied orbital in the radical anions.