50. Intramolecular Electron Spin Transfer between Naphthalene π-Systems Separated by a Variable Number of Spirobonded Cyclobutane Rings. An ESR and ENDOR Study

by **Fabian Gerson***, **Walter Huber** and **William B. Martin, Jr.**[1])

Physikalisch-Chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

and **Paul Caluwe, Tim Pepper** and **Michael Szwarc***[2])

College of Environmental Science and Technology, State University of New York, Syracuse, New York 13210, U.S.A.

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Summary

The radical anions of the compounds **N1N, N3N** and **N5N,** in which two naphthalene π-systems are separated by 1, 3 and 5 spirobonded cyclobutane rings, respectively, and that of the reference compound **N1,** containing one naphthalene π-system and one cyclobutane ring, have been studied by ESR and ENDOR spectroscopy under a variety of experimental conditions. The intramolecular electron spin transfer between the two π-moieties in **N3N**$^{\overset{\cdot}{-}}$ and **N5N**$^{\overset{\cdot}{-}}$ is slow on the hyperfine time-scale, irrespective of the applied conditions. It is also slow in **N1N**$^{\overset{\cdot}{-}}$, except for media of high solvating power. In such media, with a slight reduction of **N1N** to its radical anion, a paramagnetic species is observed, the hyperfine data of which are consistent with **N1N**$^{\overset{\cdot}{-}}$ undergoing a fast intramolecular electron spin transfer. The ESR and ENDOR spectra of this species are superimposed on those characteristic of a slow transfer. It is suggested that the fast and slow transfer involve the *syn-* and *anti-*conformations, respectively, since the distance, r, between the two naphthalene π-systems of **N1N**$^{\overset{\cdot}{-}}$ is considerably shorter in the former than in the latter ($r = 740$ *vs.* 880 pm for the distance between the centres of the π-systems). Glassy solutions of exhaustively reduced **N1N** display signals of the dianion triplet state, whereas no such signals are found for **N3N** and **N5N.** The zero-field splitting parameter, D, is 4.7 mT, corresponding to $r \approx 840$ pm.

Introduction. – Paramagnetic species are suitable model systems for investigations of the electron transfer and its dependence on the distance, r, between the donor and acceptor, since an unpaired electron spin is a convenient label by which the displacement of the electron can be monitored. The tool of choice for such studies is ESR (and ENDOR) spectroscopy, as the frequency, k, of the electron spin transfer lies in many

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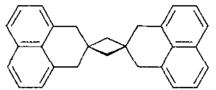
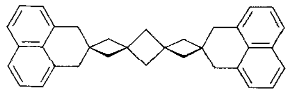
[1]) Permanent address: Department of Chemistry, Union College, Schenectady, New York 12309, U.S.A.

[2]) Present address: 1176 Santa Luisa Drive, Solana Beach, California 92705, U.S.A.

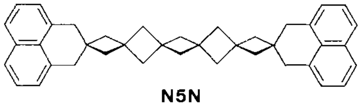
cases within the hyperfine time-scale (10^6 to 10^8 s^{-1}). The favourite species investigated are radical anions containing two equivalent π-moieties embedded in a relatively rigid framework of sp^3-hybridized carbon atoms [1–3]. In a radical anion of this structure, the π-system housing the unpaired electron represents the donor, while the second π-system acts as the acceptor. Observation of the 'true' frequency, k, of such an *intra*-molecular electron spin transfer requires that special attention must be paid to experimental conditions. First of all, it is essential to use solvents of high solvating power, so that association of the radical anion with its positively charged counterion (ion pairing) is very loose; otherwise the frequency k is tied in with the substantially lower rate of the concomitant migration of the cation between its preferred sites at each of the two π-systems. Secondly, the neutral compound, from which the radical anion is usually generated by the uptake of an additional electron, should be reduced to only a limited extent. More advanced reduction not only can forward the ion pairing (by increasing the number of counterions), but it also leads to the formation of the dianion in which both π-systems bear a negative charge. Thirdly, the initial concentration of the neutral compound itself must be reasonably low, since, in the presence of a large number of unreduced molecules, the *inter*molecular electron transfer from the radical anion to such diamagnetic species becomes competitive with the intramolecular transfer.



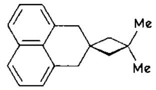
N1N



N3N



N5N



N1

In the present paper, we report on the ESR studies of the radical anions and dianions of the compounds **N1N**, **N3N** and **N5N** which differ by the number (1, 3, and 5, respectively) of the spirobonded cyclobutane rings between two naphthalene π-systems. In addition, the radical anion of the reference compound **N1**, containing one naphthalene π-system and one cyclobutane ring, has been studied.

In all four molecules, the *peri*-positions of the naphthalene moieties are linked to the cyclobutane rings by methylene groups and thus form part of a perinaphthane-like six-membered half-saturated ring which can adopt two conformations. Whereas these conformations are equivalent in **N1**, they structurally differ in **N1N**, **N3N** and **N5N**. From *Fig. 1*, in which the two conformations are schematically drawn for **N1N**, it is evident that the distance, r, between the two naphthalene π-systems is larger in the conformation denoted *anti* than in its *syn*-analogue. This difference in r decreases with the lengthening of the molecules, *i.e.*, on going from **N1N** to **N3N** and to **N5N**, as shown below by the values r estimated for the distances separating the centres of the π-systems *(cf. Fig. 1)*.

	N1N	N3N	N5N	
syn	740	1190	1640	pm
anti	880	1280	1710	pm

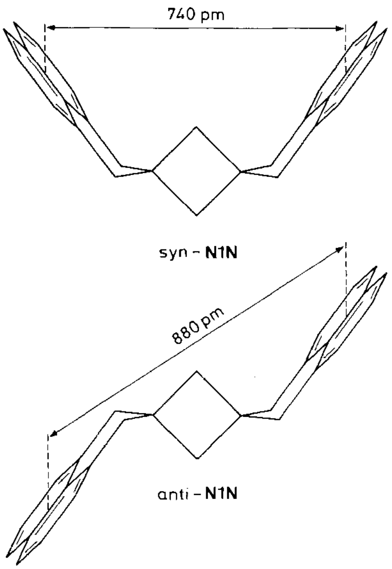


Fig. 1. *Schematic representation of the* syn- *and* anti-*conformation of* N1N

Of the numerous papers published in the past two decades on the intramolecular electron spin transfer [1–3], the most pertinent one to the present work is a study on the radical anion of *trans*-1,4-bis(α-naphthylmethyl)cyclohexane [2a] in which two naphthalene π-systems are separated by a distance r of *ca.* 900 pm. Under favourable experimental conditions (see *above*), the intramolecular electron spin transfer becomes perceivable in the ESR spectra of this radical anion above 258 K.

Results. – *Radical Anions.* The radical anions **N1**$^{\cdot-}$, **N1N**$^{\cdot-}$, **N3N**$^{\cdot-}$ and **N5N**$^{\cdot-}$ were produced from the corresponding neutral compounds by reaction with potassium metal in 2-methyltetrahydrofuran (MTHF), 1,2-dimethoxyethane (DME) and mixtures of DME with hexamethylphosphoric-acid triamide (HMPT). In a few experiments, the compounds were also reduced to their radical anions by lithium metal in a mixture of NH_3 and HMPT. ESR studies were conducted in the temperature range of 183 to 273 K. Pure HMPT was not used as the solvent because of its relatively high freezing point. In mixtures of DME and HMPT containing large portions of the latter solvent, the persistence of the radical anions became rather low at higher temperatures.

Fig. 2 shows a high-resolution ESR spectrum of the radical anion **N1**$^{\cdot-}$ in a DME/HMPT mixture (*ca.* 1:3 by volume) at 203 K, along with the corresponding proton ENDOR spectrum. These spectra readily yield six coupling constants, each of two equivalent protons (all values in mT): $a_{H2,7} = 0.162$; $a_{H3,6} = 0.189$; $a_{H4,5} = 0.460$; $a_{H\beta,ax} = 0.836$; $a_{H\beta,eq} = 0.221$ and $a_{H\delta} = 0.032$.

The positions of the protons are specified according to the formula in *Fig. 2*. Assignments to these positions have been based on analogy with the corresponding data for the radical anion of perinaphthane [4]. The hyperfine splittings from the remaining protons, including a second pair of δ-protons, are too small to be resolved (< 0.01 mT).

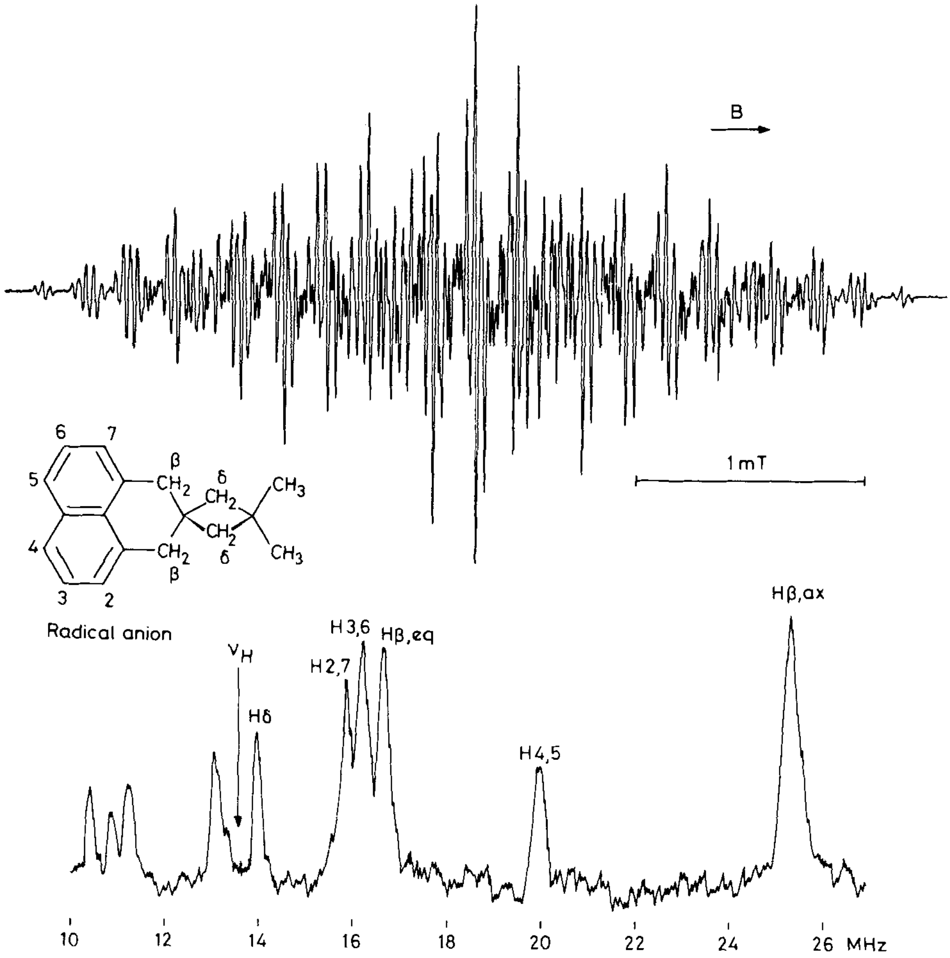


Fig. 2. *ESR and proton ENDOR spectra of* **N1**$^{\ominus\cdot}$. Solvent: DME/HMPT (1:3); counterion: K$^{\oplus}$; temp.: 203 K. ν_H = frequency of the free proton.

The spectra of **N1**$^{\ominus\cdot}$ were not very sensitive to changes in the solvent and the counterion, nor did they exhibit a pronounced temperature dependence. The latter finding indicates that conformational interconversion of the partially saturated six-membered ring fused to the naphthalene *peri*-positions must be slow on the hyperfine time-scale below 273 K.

ESR and ENDOR spectra of **N3N**$^{\ominus\cdot}$ and **N5N**$^{\ominus\cdot}$ closely resembled those taken of **N1**$^{\ominus\cdot}$ under the same conditions, and the observed proton coupling constants were, within the limits of experimental error (±1%), equal to those found for **N1**$^{\ominus\cdot}$. These statements also hold for **N1N**$^{\ominus\cdot}$ with a notable exception. When diluted solutions of **N1N** in mixtures of DME and HMPT, containing an excess of the latter solvent, were brought into a brief contact with potassium metal, the resulting radical anions gave rise

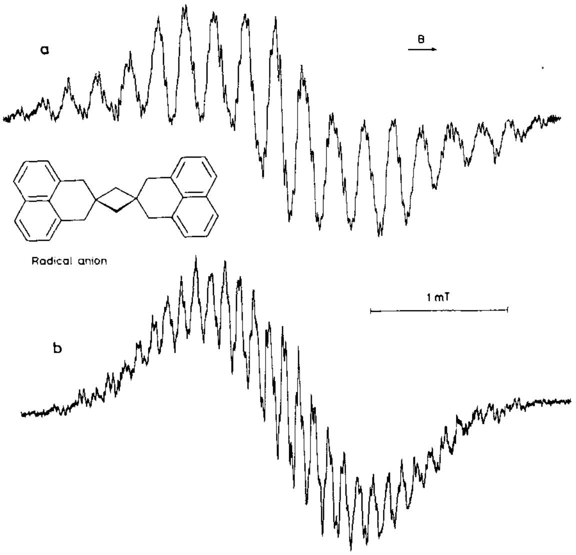


Fig. 3. *ESR spectra of* N1N$^{\dot{\ominus}}$, *taken after a short exposure of the solution to the metal mirror.* Solvent: DME for *a* (top) and DME/HMPT (1:3) for *b* (bottom); counterion: K$^{\oplus}$; temp.: 253 K.

to ESR spectra exhibiting new features. These spectra displayed additional groups of lines interposed half the way between those generally observed for **N1N**$^{\dot{\ominus}}$. The intensity of these intermediately positioned groups of lines slightly increased on raising the temperature; more critically, it depended on the conditions employed in a particular experiment, especially on the extent of reduction of **N1N**. *Fig. 3b* reproduces an ESR spectrum obtained in a typical experiment for the radical anion in a 1:3 mixture of DME and HMPT at 253 K. This spectrum is compared with that in *Fig. 3a,* taken after a brief exposure of **N1N** to the potassium mirror in pure DME at the same temperature.

The ESR spectra exhibiting additional groups of lines (like that in *Fig. 3b*) can be fitted by superimposing on the 'normal' spectrum *(Fig. 3a)* the derivative curve of a second paramagnetic species provisionally denoted **X**$^{\dot{\ominus}}$. This species has essentially the same *g*-factor[3]) and is also characterized by six coupling constants, albeit half as large and stemming from twice as many protons. Their values (in mT), each for *four* equivalent protons are therefore as follows (experimental accuracy: ± 0.005 mT): $a_{H2,7} = 0.080$; $a_{H3,6} = 0.095$; $a_{H4,5} = 0.230$; $a_{H\beta,ax} = 0.420$; $a_{H\beta,eq} = 0.110$ and $a_{H\delta} = 0.020$. The assignments of these values will be justified in the *Discussion.*

As estimated by computer simulation, the concentration of **X**$^{\dot{\ominus}}$ in the sample giving rise to the ESR spectrum in *Fig. 3b* amounts to *ca.* 75% of the total radical concentration.

The analysis of the ESR spectra of **N1N**$^{\dot{\ominus}}$ in terms of a concurrent appearance of a second species **X**$^{\dot{\ominus}}$ with half as large proton coupling constants is supported by the use of the ENDOR technique. *Fig. 4* shows the ESR and ENDOR spectra obtained in another experiment with a *ca.* 2:1 mixture of DME and HMPT at 223 K. Proton

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[3]) The *g*-factor of **N1**$^{\dot{\ominus}}$, **N1N**$^{\dot{\ominus}}$, **N3N**$^{\dot{\ominus}}$ and **N5N**$^{\dot{\ominus}}$ is 2.0027 ± 0.0001.

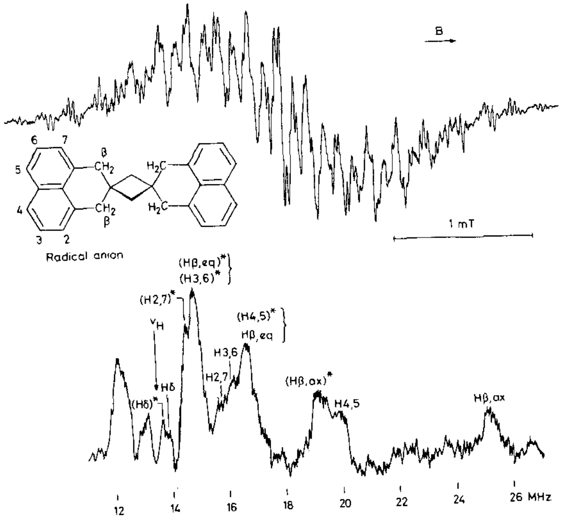

Fig. 4. *ESR and proton ENDOR spectra of* **N1N**$^{\ominus}$ *taken after a short exposure of the solution to the metal mirror.* Solvent: DME/HMPT (1:2); counterion: $K^{\oplus}$; temp.: 233 K. Protons giving rise to ENDOR signals associated with the halved coupling constants are denoted by asterisks. ν_H = frequency of the free proton.

ENDOR signals due to both 'whole' and 'halved' coupling constants are clearly present. It is interesting to note that the signals associated with the halved values and attributed to **X**$^{\ominus}$ are throughout more prominent, although the corresponding ESR spectrum suggests that the concentration of **X**$^{\ominus}$ does not exceed 50% of the total radical concentration. This finding cannot be explained solely by the higher multiplicity of the sets of equivalent protons (four *vs.* two), but must be traced to relaxation times of **X**$^{\ominus}$ favouring the ENDOR enhancement.

Occurence of **X**$^{\ominus}$ as a second paramagnetic species was also indicated by the ESR and ENDOR spectra observed upon a brief contact of **N1N** with lithium metal in a *ca.* 1:1 mixture of liquid NH_3 and HMPT.

Dianions. Glassy solutions in MTHF were studied for **N1**, **N1N**, **N3N** and **N5N** after exhaustive reduction of these compounds with potassium metal. In the case of **N1**, **N3N** and **N5N**, the ESR spectra taken under such conditions exhibited only one broad absorption; its width (*ca.* 4 mT) corresponded to the total spectral spread of the corresponding radical anions. Only in the case of **N1N**, this absorption was flanked by two pairs of signals arising undoubtedly from the triplet state of the dianion; their relative intensity increased on lowering the temperature. *Fig. 5* displays an ESR spectrum taken at 133 K. From the outer pair of the triplet signal, a *D*-value of 4.7 ± 0.2 mT was derived for the zero-field splitting parameter.

Discussion. – The finding that the ESR spectra of **N3N**$^{\ominus}$ and **N5N**$^{\ominus}$, and in general those of **N1N**$^{\ominus}$, closely resemble the spectrum of **N1**$^{\ominus}$ points to a spin *localization* on one naphthalene π-system, *i.e.*, the intramolecular electron transfer is *slow* on the hyperfine time-scale (frequency $k < 10^6\ s^{-1}$). On the other hand, the hyperfine data for **X**$^{\ominus}$ are consistent with the values expected for **N1N**$^{\ominus}$ in which the spin is *delocalized* over both π-moieties. In this case, the intramolecular electron transfer is *fast* on the pertinent time-scale ($k > 10^8$ s^{-1}). Since the radical anions are 'free' or loosely associated with their counterions in HMPT (the admixture of DME has no significant effect on the spectra, as proved by experiments in which DME is replaced by NH_3), it is unlikely that the 'localized' form of **N1N**$^{\ominus}$ differs from the 'delocalized' one (**X**$^{\ominus}$) by the tightness of ion pairing. It is rather tempting to assume that both forms have different structures. Identification of the 'localized' and 'delocalized' forms of **N1N**$^{\ominus}$ with *syn*- and *anti*-conformations, respectively, suggests itself, as the distance, *r*, between the centres of the naphthalene π-systems is considerably shorter in the former (740 pm) than in the latter (880 pm) *(cf. Fig. 1)*. For **N3N**$^{\ominus}$, **N5N**$^{\ominus}$, as well as for **N1N**$^{\ominus}$ under conditions of slow intramolecular electron spin transfer, both conformations are expected to yield identical spectra.

The zero-field splitting parameter D of 4.7 mT, found for the triplet state of the dianion of **N1N** corresponds to a distance r of 840 pm, according to the relationship $D = 2.78 \cdot 10^9/r^3$ where D is in mT and r is in pm [5]. Using this relationship, one predicts D-values of 1.5 ± 0.2 and 0.6 ± 0.1 mT for a triplet state of the dianions of **N3N** and **N5N**, respectively. The signals in question would clearly be masked by the central absorption *(cf. Fig. 5)*. Presumably, the dianions of **N3N** and **N5N** are biradicals with only slight interaction between the two unpaired electrons, each residing on one naphthalene π-moiety. Further studies are planned to elucidate the structure of all three dianions, in particular the multiplicity of their ground states.

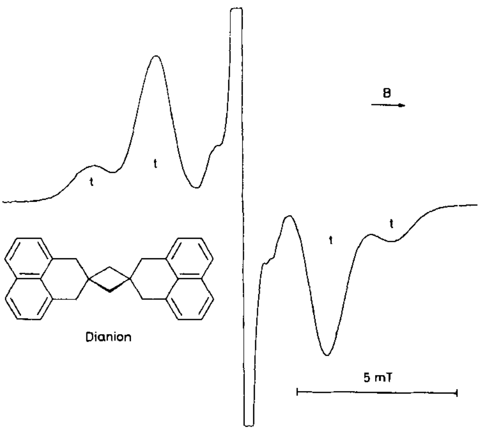

Fig. 5. *Glass ESR spectrum of an exhaustively reduced* **N1N**. Solvent: MTHF; counterion: K$^{\oplus}$; temp.: 133 K. The triplet state signals of the dianion are marked by t.

Concluding Remarks. – The results of ESR and ENDOR studies presented above enable one to estimate the upper limit for the distance r at which the intramolecular electron spin transfer between two aromatic hydrocarbon π-systems is still observable on the hyperfine time-scale (10^6 to 10^8 s^{-1}). This estimate, 700–900 pm, is compatible with the results of a previous similar investigation on the radical anion of *trans*-1,4-bis(α-naphthylmethyl)cyclohexane [2a].

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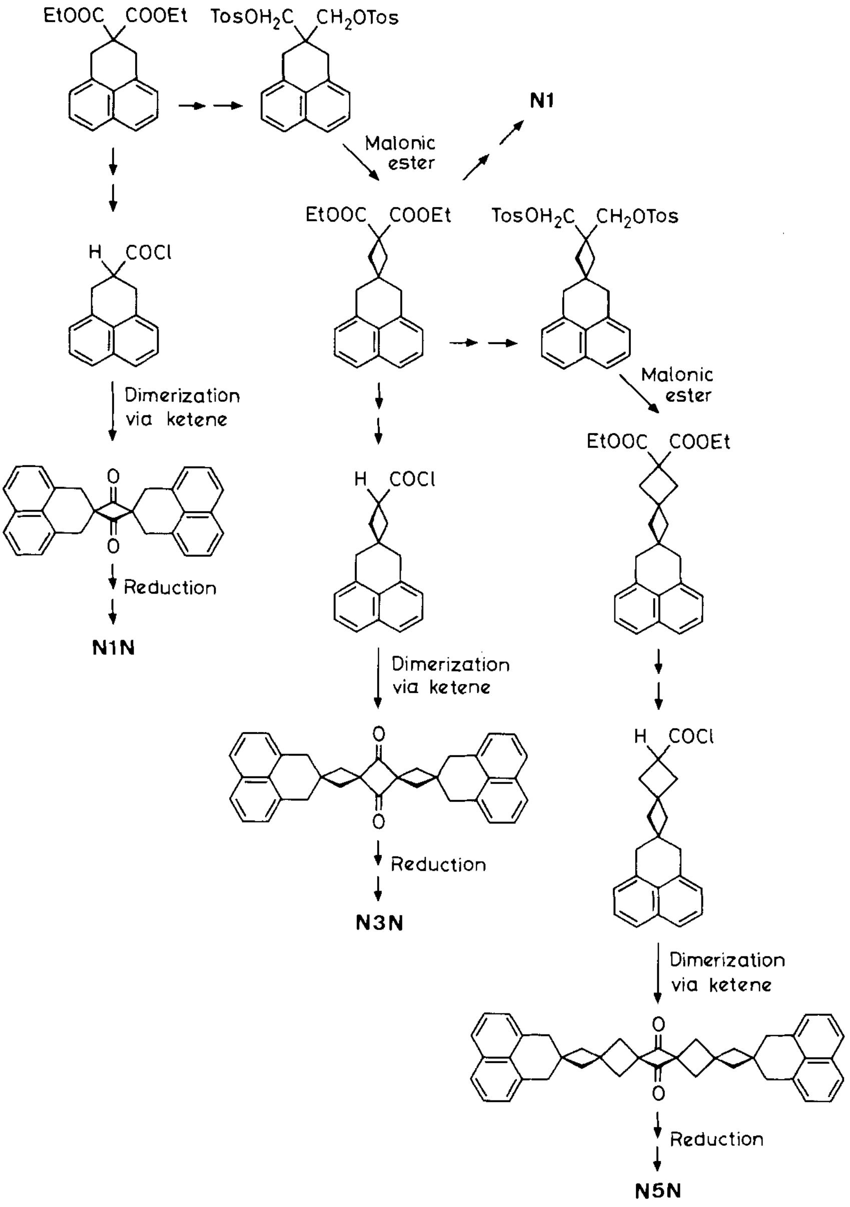

Experimental. – *Synthesis of the Compounds.* Full experimental details for the synthesis of **N1**, **N1N**, **N3N** and **N5N** will be available in [6]. An outline is given above in the reaction scheme which presents the most important steps.

The starting material was diethyl 1,2-dihydrophenalene-2,2-dicarboxylate [7]. Two complementary methods were applied to the construction of the cyclobutane rings. One of them made use of ditosylates, obtained from dicarboxylates ($LiAlH_4$, TosCl). When reacted with malonic ester, the ditosylates underwent a ring closure, yielding spirocyclic annelated dicarboxylates [8] which could further be converted into new ditosylates for the formation of an additional ring. The second method served for the final ring construction step in the synthesis of the symmetric compounds **N1N**, **N3N** and **N5N**. It involved the conversion of dicarboxylates into carbonyl chlorides (hydrolysis, decarboxylation, thionyl chlorides) and subsequently into ketenes (Et_3N). These dimerized to 1,3-cyclobutane-diones which were reduced to the corresponding hydrocarbons (thioketalization, *Raney*-Ni desulfurization).

Instrumental. The spectra were taken on a *Varian-E9*-ESR-spectrometer with an attached *Varian*-ENDOR-*1700* System.

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