

Structure of poly-(1,5-diaminonaphthalene) (1,5-DAN). A theoretical approach

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Abstract

The polymer of 1,5-diaminonaphthalene (1,5-DAN) was studied in several ways but there are still many doubts about its exact molecular structure and associated behaviour. We carried out a theoretical simulation of different proposed structures in order to elucidate the correct one. We obtained interesting results that showed some characteristics of the macroscopic behaviour. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The electrosynthesis of conducting polymer thin film electrodes is an interesting research area, because they have many applications in several scientific and technological fields. For example, electrodes coated with polyaniline films are used in batteries [1,2], gas separating membranes [3], biosensors [4] and electronic devices [5]. In addition, polypyrrole films have been used as transparent anodes for diodes [6], as fluorophore [7], and they have also been used in metal-oxide-semiconductor devices [8].

These applications have prompted studies of the electropolymerisation of mono- and polynuclear aromatic hydrocarbons containing hydroxy or amino groups such as *o*-amino phenol [9,10], 5-amino-1-naphthol [11], 1-pyrenamine [12] and naphthylamine [13–16]. Other aromatic compounds containing two –NH₂ groups such as *o*-phenylenediamine [17], 2,3-DAN [18], 1,8-DAN [19] and 1,5-DAN [20,21] have also been studied. Conducting films of these materials can be obtained potentiodynamically by oxidation of monomers in acetonitrile or aqueous solutions.

Jackowska and co-workers [20,21] performed electropolymerisation of 1,5-DAN and proposed several possible molecular structures for the polymer that was formed. They

support their conclusions mainly by IR analysis. Previously, we had carried out some experimental work along the same lines and had obtained some interesting results that complement the work of the above authors. This information was used in the theoretical calculation study of the molecular structure and IR spectra. The aim of this contribution is to afford new suggestions about the molecular structure of these polymeric materials.

2. Methodology

All calculations were performed using the hybrid B3LYP/6-31G** method [22], which combines the exact Hartree–Fock exchange with Becke's [23] and uses the Lee–Yang–Parr correlation function [24] in order to include the most important correlation effects. The version used was that included in the GAUSSIAN98 [25] package. The IR spectra simulation and thermochemistry data were obtained by frequency calculations at the same level. Initial geometries were obtained using the Universal 1.01 Molecular Mechanics method [26] from the CERIUS software [27].

This choice of calculus was based because recent investigations have demonstrated that the DFT-B3LYP method leads to excellent results for geometries and energies [28,29]. We performed a test and found the results to agree well with the previously obtained results for a similar

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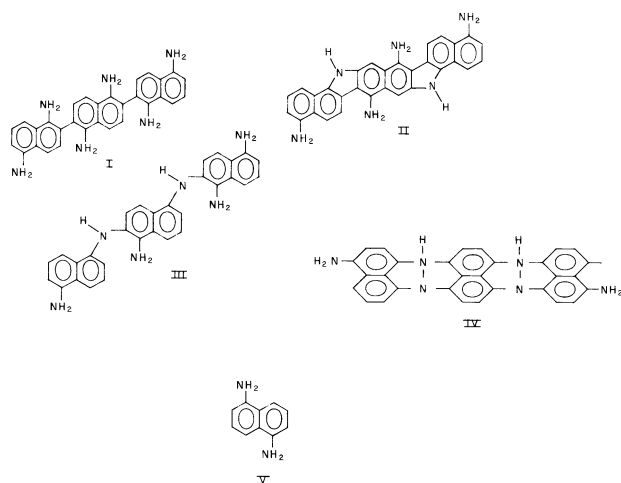


Fig. 1. Molecules under study.

molecule, the 1,5-bis(dimethylamino) naphthalene yield-653.503 a.u. as was previously reported [30].

3. Results and discussion

The possible structures analysed in this study are shown in Fig. 1. They correspond to those suggested by Jackowska [20], with the exception of molecule V that is a monomer of 1,5-DAN. All the above structures are trimers of discrete items. Molecule I is the expected compound when the monomers are joined by a simple C–C bond formation between two rings; molecule II presents the same bond but in addition also shows the C–N–C bond that forms a new ring; molecule III has the bond through a nitrogen atom, IV contains two nitrogen bonds between discrete units and V is used only as a reference for the spectroscopic and frontier orbital analysis.

This group of molecules is not, strictly speaking, isomers due to the existence of various possibilities of bonding. As suggested by Jackowska, the diverse bonding possibilities involve the loss of different numbers of hydrogen atoms. In this sense, I and III are isomers within the trimer set (~470 mol wt), while II and IV are conformational isomers (~466 mol wt). And V is the monomer of 1,5-DAN. This lack of isomerism has consequences for this study because differences in energy cannot be attributed totally to differences in conformation. This last item can be roughly estimated using the values of the total energy for each molecule,

Table 1
Total energy and corrected energy for the molecules under study

Molecule	U_{tot} (eV)	U_{corr} (eV)
I	-40251.305	-40187.596
II	-40185.578	-40185.578
III	-40251.664	-40187.956
IV	-40180.789	-40183.789
V	-13438.631	

the values obtained using this estimation are given in Table 1. To facilitate a comparison of these data, we normalised the results by subtracting the energy values of the hydrogen atoms (calculated on single atom at the same level of theory) from that of the related atom of the molecules having lower molecular weight, and determining quantities that can be compared. The corrected energies are also shown in Table 1.

In a very rough approximation, we can consider that I and III are the energetically favoured species because they have

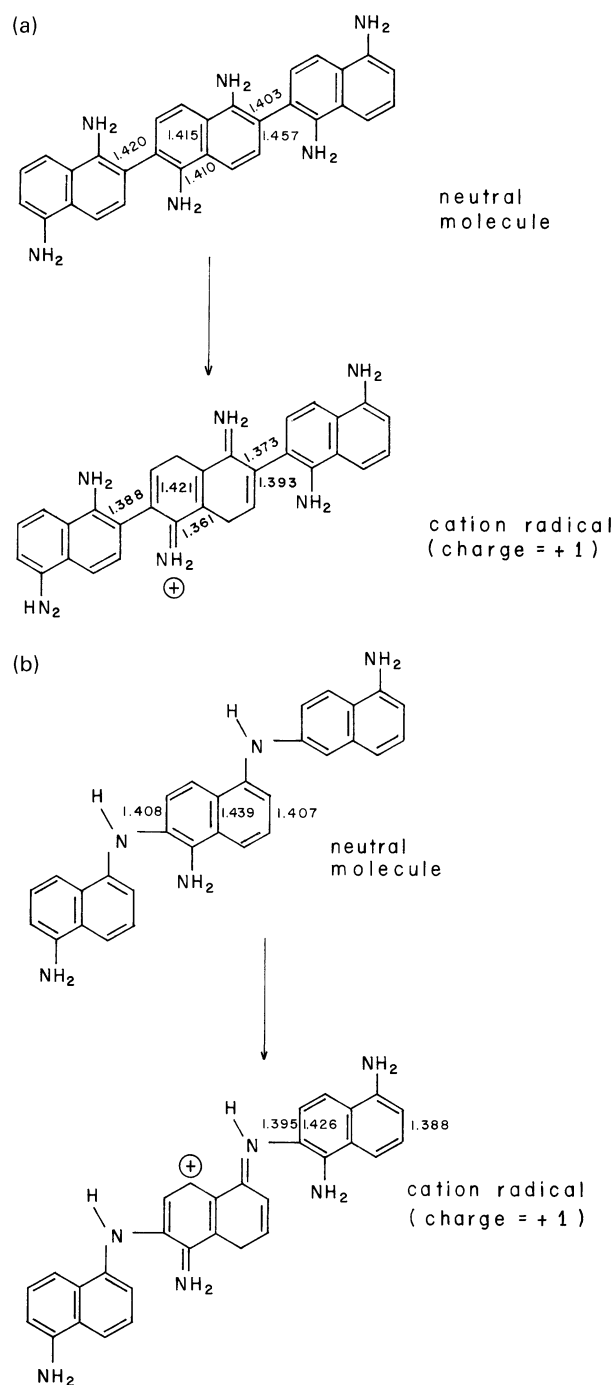


Fig. 2. Evidence of quinoid form for (a) molecule I and (b) molecule III.

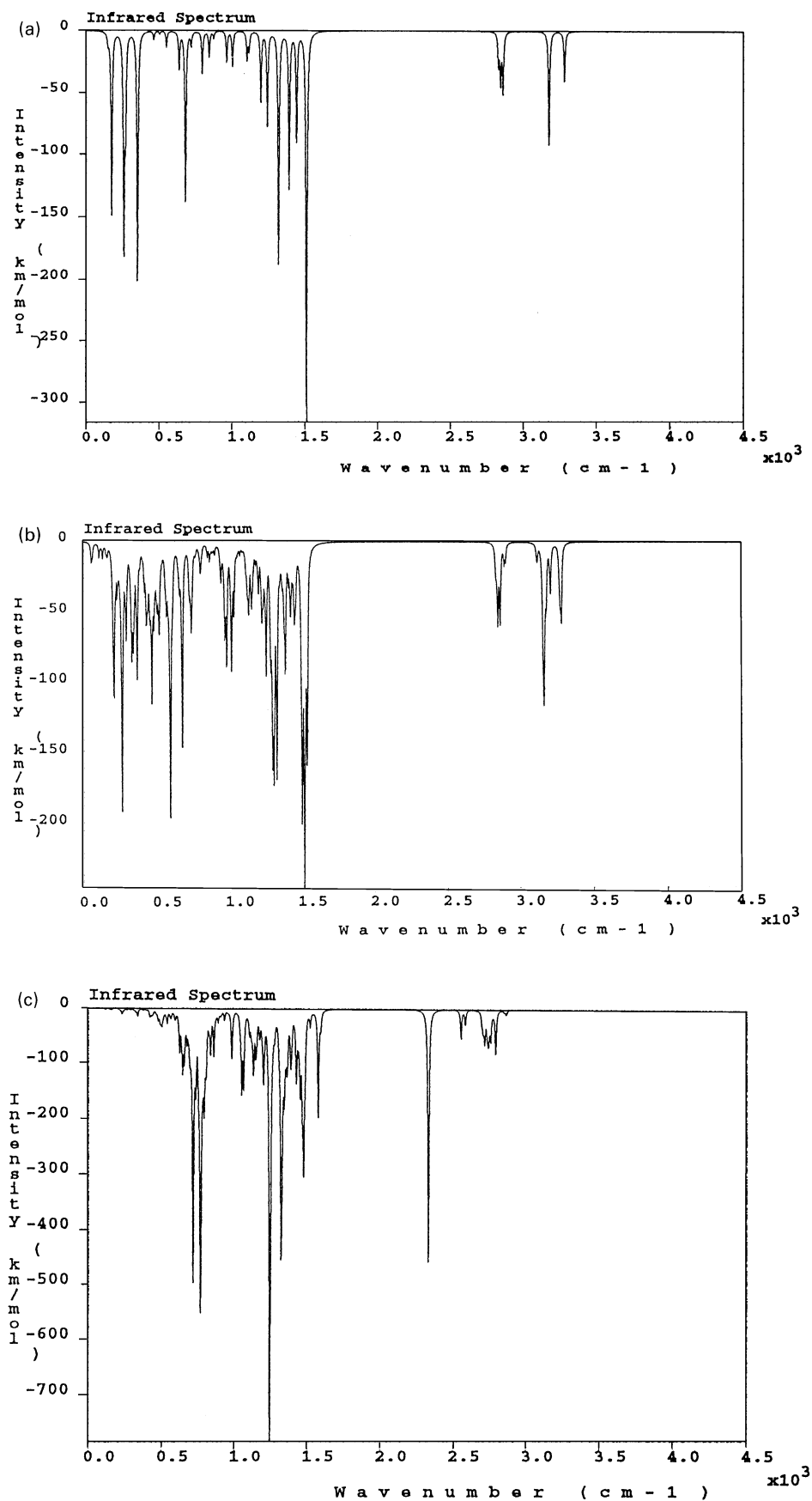


Fig. 3. IR spectra of (a) compound V, (b) compound I and (c) compound III.

the lowest energy values, with a difference of ~ 0.36 eV (8.301 kcal mol $^{-1}$) between them. The interesting feature is that they are the only species that do not present cyclisation between two naphthalene units and have no net charge. It can be considered that the formation of such cycles adds some tension to the polymer chains and this increases the energy. In the case of II, the increase is small and the difference with respect to III (~ 2.38 eV) makes this compound available, but in the case of IV the difference is dramatic (~ 7.167 eV) and it is unlikely that this species can exist.

It has been suggested that for polyaniline [31], the electropolymerisation of the conductive substance should imply the formation of a polaron that leads to the formation of quinoid rings in the chain. This possibility is analysed in our case by calculating the structure of the corresponding radical-cation items. These kinds of calculations were performed on the optimised geometries of neutral molecules in order to look for new structures in which a quinoid ring might appear. The results for two of the molecules are shown in Fig. 2 indicating the relevant changes of the bond distances that imply the formation of a quinoid ring.

A shortening in the lateral bonds of the central naphthalene group is appreciated for two cases, i.e. I and III. Cases II and IV do not show relevant change. The shortening suggests the formation of new forms for the first two structures that include a quinoid ring joined to an aromatic one in the middle of each molecule. The important topic to analyse here is that I and III can develop the structure suggested for a polaron, as in the case of polyaniline, but only with an excitation to help them reach the charged radical species. There are several experimental methods that allow the preparation of these kinds of conductive polymers.

A new comparison among energy data was made on the cation radical species and the results, with the correction for different number of hydrogen atoms, are shown in Table 2.

We found a similar behaviour to that of the neutral molecules. II and IV seem to be molecules that would be hard to obtain, but the difference between I and III was significantly smaller than in Table 1 (~ 0.255 eV). This is a very interesting result because Jackowska [20] concluded on the basis of IR evidence that these two structures should be found as a mixture in the electropolymerisation reaction. This phenomenon should occur when the resultant polymer is doped in order to produce the cation radical fragments, and finally the polaron. At this point, we consider that it is useful to compare the theoretical and experimental IR spectra.

Table 2
Energy for cation radical species

Molecule	U_{corr} (eV)
I	-40182.299
II	-40181.765
III	-40182.554
IV	-40180.003
V	-13431.235

Fig. 3 shows the theoretical IR spectra of the monomer and trimer molecules I and III; in the first case, a calculated correction scale factor of 0.95 was applied, 0.98 for the second and 0.94 for the third as suggested for this method [32]. The analysis of these showed that they are very similar to the experimental spectrum. Jackowska indicated that there are three main bands at 3230, 3330 and 3415 cm $^{-1}$ corresponding to the symmetric and antisymmetric NH $_2$ stretching vibrations in the monomer spectrum. These three bands also appear in the monomer theoretical spectrum and in that of the trimer I. However, the strong differences in the intensities (favouring compound I) indicating that there are free terminal NH $_2$ groups in this last case; as is known from the molecular structure. An interesting feature is the appearance of new bands, as suggested by Jackowska, at 1210 and 1467.5 cm $^{-1}$ for the C–C stretching in I and at 1377 and 1501 cm $^{-1}$ corresponding to the –NH– group in III. Thus, if both bands are seen in the experimental spectrum then, both species must be present in the experimental item.

The arguments presented in the last paragraph strongly suggest that the polymer of 1,5-DAN should be formed by chains arising from both the chemical species, one with C–C bonds between aromatic groups and the other with –NH– units in the same place. Thus, both possibilities should be accessible for the monomer in the context of a polymerisation reaction. In this sense an analysis of the frontier orbitals of the monomer can be useful.

The logical pathway for the polymerisation of 1,5-DAN is within the context of an electrophilic aromatic substitution. The monomer should take one of the two configurations of a cation in order to form a Wheeland intermediate, and follow a propagation reaction; these configurations are shown in Fig. 4.

However, these are resonant isomers; the shape of the HOMO of V (see Fig. 5) indicates that there are possibilities for allocating the positive charge in the nitrogen atom as well as in the carbon atom in the *ortho* position with respect to the amino group (or even in *para* position), and therefore both species should be obtainable.

This last argument implies that both the Wheeland intermediates should be found in the bulk of the electropolymerisation reaction. Thus, polymers with chains based on I and III structures should be formed as was suggested by

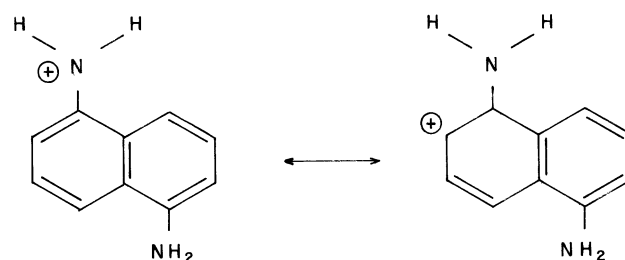


Fig. 4. Wheeland configurations for compound V.

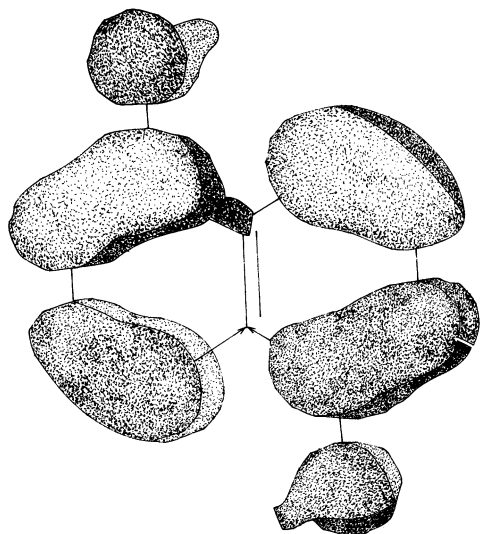


Fig. 5. HOMO of molecule V.

the analysis of the IR spectra, and was claimed for by Jackowska and coworkers [20].

There is another less relevant result from these calculations concerning the spatial conformation of the involved species. Molecules I and III present different shapes (see Fig. 6), molecule I has a quasi-linear conformation and it

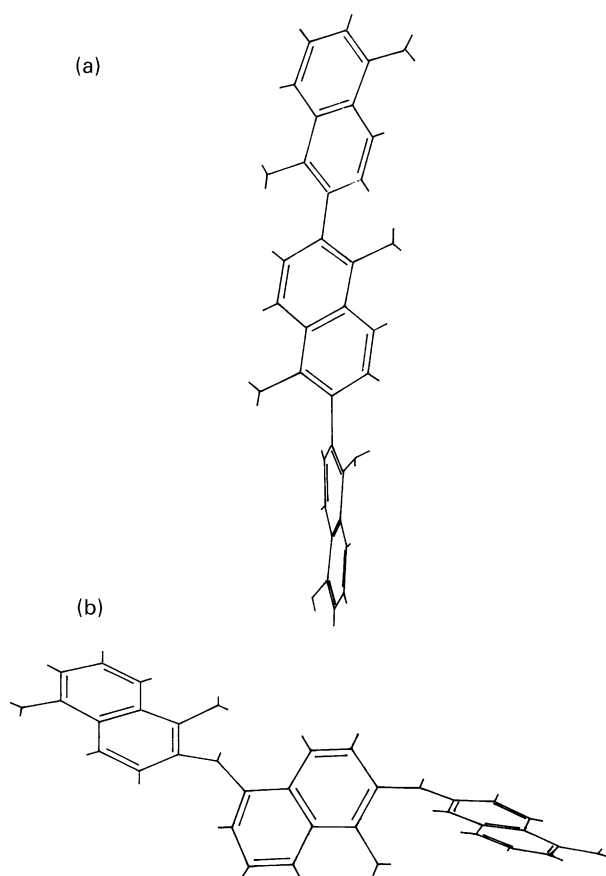


Fig. 6. Spatial shape of (a) molecule I and (b) molecule III.

would be planar if the free rotation between the rings could be precluded. Meanwhile, molecule III has a tendency to adopt a helical shape. This topic would be important if the molecules were obtained as crystals, but as yet they have been obtained and studied as films or in solution.

4. Conclusion

The polymer obtained by the electropolymerisation process from the monomer 1,5-DAN, was studied in a theoretical manner in order to elucidate the molecular structure. The energy results allow us to suggest that there are only two possibilities for bonding: a direct link between the two rings (C–C bond) or a link throughout the formation of an –NH– bond. This argument is confirmed by the analysis of the corresponding cation-radical species and by the comparison of the theoretical IR spectra with the experimental spectra obtained by Jackowska and co-workers. The possible reaction pathway is analysed via an electrophilic aromatic substitution reaction and the probability of formation of the Wheeland intermediate for both structures is assessed.

Acknowledgements

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