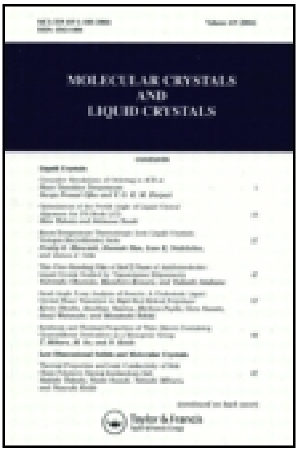


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Ability of Substituted Perylenes to Form Organic Conductors

Luis F. Veiros [a] & Jorge Morgado [a]

[a] Dep. Eng. Química, Instituto Superior Técnico, Av. Rovisco Pais, P-1049-001, Lisboa, Portugal

To cite this article: Luis F. Veiros & Jorge Morgado (1999): Ability of Substituted Perylenes to Form Organic Conductors, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 333:1, 259-268

To link to this article: http://dx.doi.org/10.1080/10587259908026009

Mol. Cryst. Liq. Cryst., Vol. 333, pp. 259-268
Reprints available directly from the publisher
Photocopying permitted by license only

Ability of Substituted Perylenes to Form Organic Conductors

LUIS F. VEIROS* and JORGE MORGADO

Dep. Eng. Química, Instituto Superior Técnico, Av. Rovisco Pais, P-1049–001 Lisboa, Portugal

(Received October 01, 1998; In final form February 03, 1999)

The changes on the frontier orbitals of perylene upon substitution of the hydrogen atoms by sulfur or short alkyl groups in several positions are analysed. A qualitative discussion on the importance of such changes in the ability of the resulting compounds to originate one-dimensional organic conductors of the radical-cation salts type, is presented. Perylene and perylene derivatives, previously used in the preparation of organic conductors, are used as a guiding reference.

Keywords: Perylene; Sulfur Substituted Perylenes; Electron Donors; Conductor

1. INTRODUCTION

The properties of crystalline organic conductors depend not only on the electronic characteristics of the active molecules used in their preparation but also on their arrangement in the final structure. If we consider, for instance, the radical-cation salts type, we can investigate the ability of the electron-donor molecules to give rise to an electronic pathway, considering the overlap of the frontier orbitals, usually HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital).

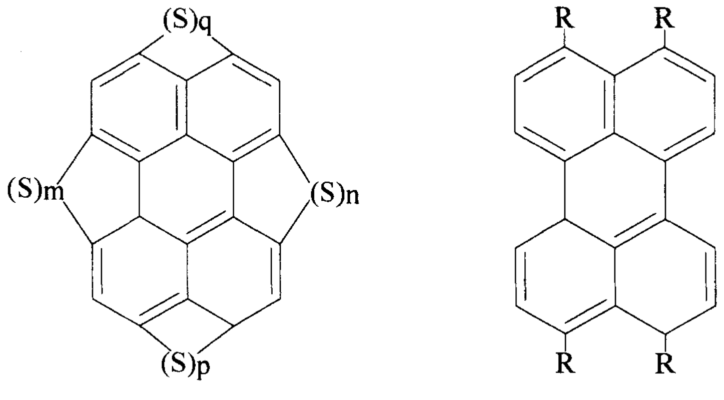
Perylene (Per = $C_{20}H_{12}$) was one of the first electron donor molecules used in the preparation of organic conductors and it is still widely used in our laboratory [1–4]. In addition, several reports appeared on the properties of conducting materials based on perylene derivatives [1, 5–10].

Among the conductors prepared with perylene the ones that show the most typical metallic-like properties are those of the family α-$(Per)_2M(mnt)_2$ [1–4].

---

* Correspondence Author.

Among those based on its derivatives, $CPP_2(I_3)_{1-\delta}$ and TTP-$I_{1.28}$ are the best conductors (CPP = tetrahydrodicyclo-pentaperylene, TTP = tetrathioperylene; see fig. 1). The bandwidths of both α-$(Per)_2M(mnt)_2$[11] and CPP_2 $(I_3)_{1-\delta}$ [10] are close to 0.6 eV. The bandwidth of TTP-$I_{1.28}$ was not calculated given the limited crystallographic data [6].



A

B

E-TTP: m=n=2, p=q=0

PET: n=1, m=p=q=0

TTP: p=q=2, m=n=0

CPP: R-R = $-CH_2-CH_2-$

DEP: R-R = -CH=CH-

TMP: R = $-CH_3$

FIGURE 1 Molecular structure and used name abbreviations of the perylene derivatives having either sulfur (A) or alkyl groups (B) replacing hydrogen atoms

The conduction band of one-dimensional (1-D) perylene-based molecular conductors is usually the result of the overlap between the HOMO of the donor molecules (perylene) along a stack [11]. Since the perylene molecules in these solids act as electron-donors, their HOMO become partially empty, being able to form a metallic band if the geometrical arrangement of the molecules in the crystal structure is appropriate. The resulting bandwidth may be enlarged by superposition with the closest bands, such as the LUMO and the SOMO (second occupied molecular orbital). However, this is not usually the case for the perylene-based solids, given the small bandwidths typical of these materials.

Here, we report on molecular orbital calculations of the extended Hückel type [12, 13] on several perylene derivatives and discuss the potential use of these compounds for the preparation of conductors of the radical-cation salts type. Given the limitations of the method used, we only aim at a qualitative reasoning, although well based in the known examples of perylene and perylene derivative 1-D conductors. In fact, of all the twelve perylene derivatives presented, five are known, and correspond to published 1-D molecular conductors. These can be taken as a calibration to the general approach followed in this work.

The final crystalline arrangement in these solids is difficult to predict. Therefore, we will not discuss the implications of the substituents introduced into the perylene molecule on the crystalline arrangement, which obviously renders to the conclusions some degree of uncertainty. The presence of substituents on the donor molecule, even when they do not have an active role in the frontier orbitals, can have a determinant influence on the final arrangement and, therefore, on the interaction between the frontier orbitals within the crystal. In particular, for these solids, the interactions between donor molecules are weak, of the long range type, and therefore very sensitive to changes on the distance and orientation.

Another aspect which is not considered here is the possible change in the electron donation ability of a molecule upon inclusion of substituents. The presence of polarizable substituents (such as sulfur or selenium) can facilitate the oxidation and, in case they contribute to the HOMO, it is known they can also lead to a decrease of the repulsion energy between electrons and an increase of the bandwidth [14].

All these limitations taken into account, this contribution should only be regarded as a broad guideline to potentially interesting perylene derivatives as building units in new molecular conductors of this family.

2. RESULTS AND DISCUSSION

The approach used in this study comprises two steps: First, we analyse the effect of substituents on the frontier levels of perylene, especially on the HOMO, since these derivatives are intended to be used as electron-donors. In a second step, we analyse the possibility of obtaining a delocalised band which could support a metallic-like charge transport. The derivatives analysed in this study can be represented by the general structures shown in fig. 1, in which are also shown the abbreviations used through the text.

The electronic pathway in the perylene-based conductors is associated to the band resulting from the HOMO overlap between neighbour molecules along a stack, $(\mathrm{Per})_n$. For instance, for the α-$(\mathrm{Per})_2\mathrm{M(mnt)}_2$ family of compounds [1–4] a band having a width of 0.5–0.6 eV [11] is typically obtained, which is responsible for the metallic-like properties they exhibit. The HOMO of the perylene molecule is show in fig. 2A.

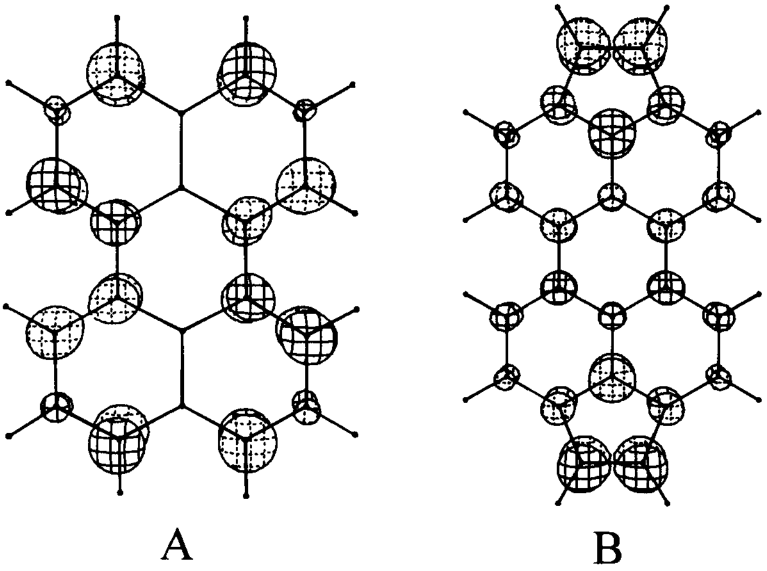


FIGURE 2 A: HOMO of perylene; B: HOMO of dietheneperylene, DEP (fig. 1B: R—R = -CH=CH-)

Sulfur based derivatives

Two sulfur derivatives of perylene, perilothiophene, PET, (fig. 1A: m=p=q=0, n=1) [5] and tetrathioperylene, TTP, (fig. 1A: p=q=2, m=n=0) [6] were previously used as electron donors in the preparation of organic conductors.

The HOMO of PET is similar to that of perylene (see fig. 2A), with no contribution from the sulfur atom. The calculated bandwidth (W=0.57 eV) [5] is similar to the ones found for the α-$(Per)_2M(mnt)_2$family of compounds.

For TTP, however, the outer sulfur atoms have strong contributions to the HOMO, as shown in fig. 3A. Thus, TTP is a good electron-donor candidate to form 1-D conductors upon stacking. This result agrees with the conductivity measurements on the solid $(TTP)I_{1.28}$, although the experimental data was somehow obscured by the poor quality of the crystals [6]. This prevented the full determination of a crystal structure and, consequently, a band structure calculation.

The results of the calculations on the other sulfur derivatives (fig. 1A), not yet synthesised, are shown in Table I, with the symmetry of the frontier orbitals and

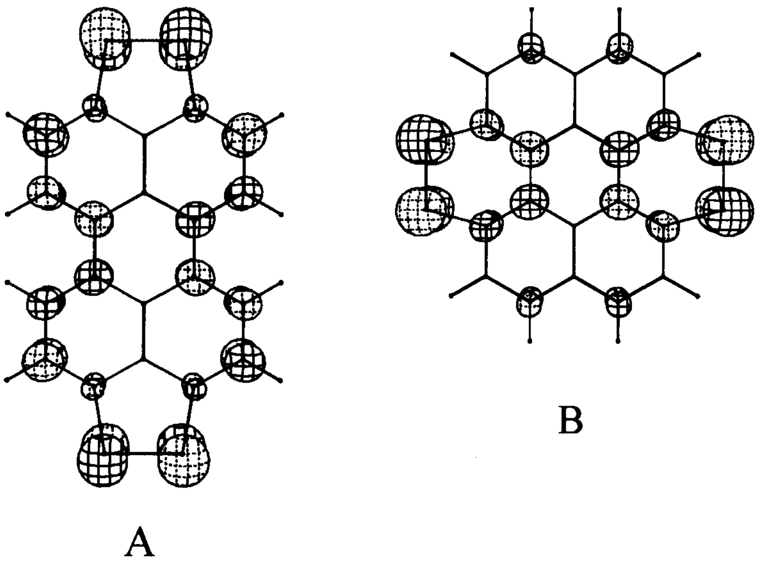


FIGURE 3 HOMO of perylene sulfur derivatives. A: tetrathioperylene, TTP; and B: E-TTP (fig. 1A: m=n=2, p=q=0)

their energy separation. Although the assumed planar geometry may be somehow less likely for some of the derivatives (*e.g.* q = 1 or p = 1; or m = n = 2, p = q = 0), they are presented for the sake of a systematic approach.

TABLE I Symmetry and approximate energy separation between the frontier orbitals for some of the sulfur derivatives shown in figure 1A

Perylene derivative (see fig. 1A)	*HOMO symmetry-type*	*SOMO symmetry-type*	*HOMO-SOMO separation (eV)*
1S-Per: m=n=q=0, p=1	σ	π	0.7
2S-Per: m=n=1, p=q=0	σ	π	0.1
2S′-Per: m=q=0, n=p=1	σ	π	0.6
3S-Per: m=n=p=1, q=0	σ	π	0.5
4S-Per: m=n=p=q=1	σ	σ	0.4
4S′-Per: m=n=2, p=q=0	π	π	0.6

Most of the sulfur derivatives mentioned in Table I have a σ-type HOMO. Therefore, the band that may arise from the stacking of these molecules is expected to be narrow and have localised electrons, due to the poor overlap between the orbitals of neighbour molecules. For the first four derivatives (having one up to three sulfur atoms), the SOMO has the adequate π-type symmetry. However, only in the case where two sulfur atoms are at the two equatorial position — 2S-Per: $m=n=1, p=q=0$ — perylodithiophene, this level is relatively close to the HOMO. In this case, a superposition between the HOMO and the SOMO bands may occur, depending on the crystal structure, and give rise to a conduction band.

In the case of the derivative having four sulfur atoms — 4S-Per: $m=n=p=q=1$ — the highest π-type occupied level is the third occupied molecular orbital, "TOMO", which lies 0.6 eV below the HOMO. It is therefore unlikely that this compound could give rise to conducting radical-cation salts.

Among the sulfur derivatives of perylene which were analysed in Table I, the most interesting is the one having four sulfur atoms, two in each side of the equatorial position — 4S'-Per: $m=n=2, p=q=0$, here named E-TTP. As found for TTP, this derivative has a HOMO level with adequate π-type symmetry (see fig. 3).

Alkyl derivatives

Organic conductors have already been obtained from tetramethylperylene, TMP (fig. 1B: $R=CH_3$) [7] and tetrahydrodicyclopentaperylene, CPP (fig. 1B: $R—R = CH_2—CH_2$) [8–10]. The HOMO of both these molecules is similar to that of perylene. If a vinylene group (-CH=CH-) is present instead of the $-CH_2CH_2-$ group of CPP, the resulting molecule, here named dietheneperylene, DEP, has also a HOMO with a π-symmetry (see fig. 2B). However, even if all the carbon atoms contribute to the HOMO, at variance with the situation found in perylene, the electron-density of this orbital is not so uniformly distributed over the molecule as in the HOMO of perylene (see fig. 2). In fact, for DEP, 40 % of the electron density of the HOMO lies on the carbon atoms of the outer -CH=CH- groups.

In a possible radical-cation salt based on DEP molecules, we can consider two extreme situations, concerning the overlap mode: (i) the geometrical overlap between neighbour molecules in the stacks is similar to the one found in the perylene solids [15–17] – a graphite-like slided mode – in which case we would expect weaker interactions than in the perylene solids, due to the lack of HOMO's electron-density in the middle part of the molecule; and (ii) a different overlap mode allowing a closer proximity of the outer -CH=CH- groups of neighbour molecules, which could contribute to an increase of the intermolecular interactions. It should be mentioned that, although the electron-density distribution of the HOMO of TTP (fig. 3A) is similar to that of DEP (fig. 2B), the overlap mode in (TTP)$I_{1.28}$ [6] is similar to that found in the highly conducting perylene-based compounds [15–17] and in CPP_2 $(I_3)_{1\text{-}\delta}$ [10], given, thus, more weight to hypothesis (i).

3. CONCLUSIONS

We have analysed several perylene derivatives in relation to the symmetry-type of the frontier levels. The goal is the search for molecules having a π-type symmetry HOMO, which could allow, upon a face-to-face stacking, the establishment of a delocalised band.

Among the investigated sulfur-containing molecules, we conclude that, with the exception of the molecules already used in the preparation of organic conductors, PET and TTP, only the substituted perylene having four sulfur atoms at equatorial positions, E-TTP (fig. 1A: m=n=2 and p=q=0) has a HOMO with the adequate type of symmetry (see Table I). The symmetric derivative having two sulfur atoms at the equatorial position (fig 1A: m=n=1, p=q=0), perilodithiophene, has a SOMO of the adequate symmetry, separated from the HOMO by an energy of 0.1 eV. This value is smaller than half the typical bandwidth of 0.6 eV found in these quasi-one-dimensional compounds. Thus, if these molecules would stack the same way as observed for perylene in the α-$(Per)_2M(mnt)_2$ [15–17], the band resulting from the SOMO interaction would be ca. 0.6 eV wide and would cross the HOMO position. This band could, upon charge transfer as in the perylene family of compounds, support charge transport.

The only compound based on PET so far characterised is $(PET)_3[Ni(mnt)_2]_2$ [5]. In this compound the PET molecules do not form a regular stacking, being grouped in trimmers. In case a regular stacking could be obtained, a bandwidth of Å 0.5–0.6 eV would be expected if we assume a PET-PET distance similar to that observed between perylene units in α-$(Per)_2M(mnt)_2$ compounds. In this case, however, even if the sulfur atom has no contribution to the HOMO, the steric hindrance and the lower symmetry it creates are likely to be responsible for the observed absence of regular stacking. It should be mentioned, however, that, contrary to perylene, PET molecules in the pure compound form nice stacks, with sulfur-sulfur interactions connecting neighbouring stacks [18].

For the alkyl-substituted perylenes (fig. 1B). in which R is an alkyl group, we expect no changes on the HOMO in relation to the unsubstituted perylene. The steric effects would therefore play a significant role in determining the interactions between the molecules in the solid.

An interesting derivative is the dietheneperylene, DEP. This has an HOMO with the right type of symmetry and should be a good candidate to form organic conductors. However, as that orbital has lower π-electron density in the middle part of the molecule than observed for the perylene, it would probably lead to a band narrower than observed for the perylene-based compounds, if the geometrical overlap is maintained.

4. SUMMARY

We have analysed the possibility of obtaining suitable perylene derivatives to be used as electron-donors in the preparation of organic conductors. These derivatives are obtained by the substitution of hydrogen atoms of perylene by either sulfur or short alkyl groups. Taking the characteristics of the reported conductors based on perylene and perylene derivatives into consideration, the π-type symmetry of the HOMO was used as a condition to be fulfilled so that a delocalised band could be obtained upon face-to-face stacking of these molecules.

Among the derivatives that were investigated the most promising ones are dietheneperylene, DEP (fig. 1B: R—R = -CH=CH-), perylodithiophene (fig. 1A: m=n=1, p=q=0), and the derivative having four sulfur atoms, two on each side of the equatorial position, E-TTP (fig. 1A: m=n=2, p=q=0).

Acknowledgements

We thank Prof. L. Alcácer and Prof. M. Almeida for their helpful discussions and comments. This work benefited from financial support from JNICT under contracts n° PRAXIS/2/2. 1/QUI/203/94 and PBIC/C/QUI/2201/95.

References

[1] M. Almeida and R. T. Henriques, in *Handbook of Organic Conductive Molecules and Polymers*, Hari Singh Nalwa (ed.), John Wiley & Sons, Chichester, 1997, Vol. 1, p. 87.

[2] M. Almeida, V. Gama, R. T. Henriques and L. Alcácer, in *Inorganic and Organometallic Polymers with Special Applications*, ed. R. M. Laine, Kluwer Academic Publications, Dordrecht, 1992, p.163.

[3] R. T. Henriques, V. Gama, G. Bonfait, I. C. Santos, M. J. Matos, M. Almeida, M. T. Duarte and L. Alcácer, *Synth. Met.* **56,** 1846 (1993).

[4] V. Gama, R. T. Henriques, G. Bonfait, M. Almeida, S. Ravy, J.-P. Pouget and L. Alcácer, *Mol. Cryst. Liq. Cryst.* **234,** 171 (1993).

[5] J. Morgado, I. C. Santos, L. F. Veiros, R. T. Henriques, M. T. Duarte, M. Almeida and L. Alcácer, *J. Mater. Chem.*, **7,** 2387 (1997).

[6] B. Hilti, C. W. Mayer and G. Rihs, *Solid State Commun.* **38,** 1129 (1981).

[7] P. Michel, A. Moradpour, P. Penven, L. Firlej, P. Bernier, B. Levy, S. Ravy and A. Zahab, *J. Am. Chem. Soc.* **112,** 8285 (1990).

[8] R. Lapouyade, J. P. Morand, D. Chasseau, C. Hauw and P. Delhaès, *J. Physique* **44,** C3–1235 (1983).

[9] P. Penven, D. Jérôme, S. Ravy, P. A. Albouy and P. Batail, *Synth. Met.* **27,** B405 (1988).

[10] J. Morgado, I. C. Santos, R. T. Henriques, M. Fourmigué, P. Matias, L. F. Veiros, M. J. Calhorda, M. T. Duarte, L. Alcácer and M. Almeida, *Chem. Mater.* **6,** 2309 (1994).

[11] L. F. Veiros, M. J. Calhorda and E. Canadell, *Inorg. Chem.* **33,** 4290 (1994).

[12] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.* **36,** 2179 (1962).

[13] R. Hoffmann, *J. Chem. Phys.* **39,** 1397 (1963).

[14] D. O. Cowan, J. A. Fortkort and R. M. Metzger, in *Lower-Dimensional Systems and Molecular Electronics,* R. M. Metzger, P. Day and G. C. Papavassiliou (eds.), NATO ASI Series, Plenum Press, New York, 1991, Vol. 248, p. 1.

[15] L. Alcácer, H. Novais, F. Pedroso, S. Flandrois, C. Coulon, D. Chasseau and J. Gaultier, *Solid State Commun.* **35,** 945 (1980).

[16] A. Domingos, R. T. Henriques, V. Gama, M. Almeida, A. Lopes Vieira and L. Alcácer, *Synth. Met.* **27,** B411 (1989).

[17] V. Gama, M. Almeida, R. T. Henriques, I. C. Santos, A. Domingos, S. Ravy and J.-P. Pouget, *J. Phys. Chem.* **95,** 4263 (1991).

[18] I. C. Santos, M. Almeida, J. Morgado, T. L. Duarte and L. Alcácer, *Acta Cryst. C* **53**, 1640 (1997).

[19] J. H. Ammeter, H.-J. Bürgi, J. C. Thibeault and R. Hoffmann, *J. Am. Chem. Soc.* **100,** 3686 (1978).

[20] C. Mealli and D. M. Proserpio, *J. Chem. Ed.* **67,** 39 (1990).

[21] M.H Whangbo, and R. Hoffmann, *J. Am. Chem. Soc.,* **100,** 6093 (1978).

[22] M.H. Whangbo, W.M. Walsh, jun., R.C. Haddon and E. Wudl, *Solid State Commun.,* **43,** 637 (1982).

[23] M.H. Whangbo, J.M. Williams, M.A. Beno, and J.R. Dorfman, *J. Am. Chem. Soc.,* **105,** 645 (1983).

Appendix

All the calculations were carried out using the extended Hückel method [12, 13] with modified H_{ij}'s [19]. Standard parameters were used for all the atoms. Only *s* and *p* orbitals were considered for S. Three-dimensional representations of orbitals were drawn using the program CACAO [20].

Bandwidths quoted along the text were calculated with the tight-binding approach [21–23] of the extended Hückel method and the same basis set was used for the study of the perylene derivatives frontier orbitals. Full descriptions of those calculations can be find in the references cited throughout the text.

The calculations were performed on model molecules with idealised planar geometries and the maximum symmetry, taken from the real structures, when available. The bond distances (Å) were as follows: C-C 1.40, C-S 1.70, S-S 1.90, C-H 1.08.