ORGANIC
LETTERS

2011
Vol. 13, No. 10
2560–2563

Synthesis and Characterization of 2,8-Diazaperylene-1,3,7,9-tetraone, a New Anthracene Diimide Containing Six-Membered Imide Rings

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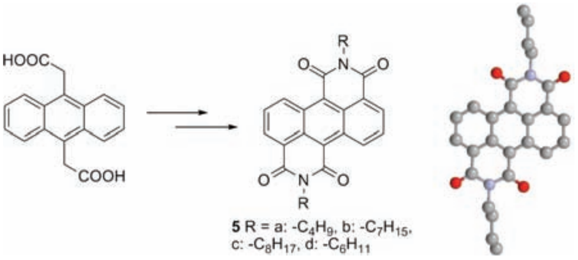
Received March 11, 2011

ABSTRACT



A successful synthesis of novel diimides, namely anthracene diimide containing six-membered imide rings, with potential application in organic electronics is reported. The single crystal of 5a exhibits a close interplanar spacing of 3.45 Å between molecules in a stack.

Aromatic polyimides are among the strongest polymeric engineering materials,[1] a prime example being Kapton. The majority of the aromatic polyimides are five-membered ring cyclic imides based on pyromellitic dianhydride (structure **1**).[1] Six-membered ring polyimides based on naphthalene and perylene are considerably more rare. Surprisingly, according to SciFinder, polyimides based on structure **5** are unknown.

Organic semiconductors have been of great research interest for use in low cost, ultrathin, and flexible products such as flexible transistors, displays, and photovoltaics.[2–5] While many p-channel organic semiconductors have been thoroughly characterized and have achieved acceptable device performance and stability, n-channel organic semiconductors are less numerous.[6] There are several examples that are being explored for the latter, such as copper hexadecafluorophthalocyanine (F_{16}CuPc),[7] C_{60} and its derivatives,[8] chemically modified oligothiophenes,[9] perfluoropentacene ($F_{14}C_{22}$),[10] and rylene diimides.[11,13] Recently, rylenes and related aromatic cores, particularly

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(1) Stevens, M. P. *Polymer Chemistry an Introduction*, 3rd ed.; Oxford University Press: Oxford, 1999; p 382.

(2) Horowitz, G. *J. Mater. Res.* **2004**, *19*, 1946.

(3) Schmidt-Mende, L.; Fechtenkotter, A.; Müllen, K.; Moons, E.; Friend, R.; Mackenzie, J. *Science* **2001**, *293*, 1119.

(4) Loo, Y.-L.; McCulloch, I. *MRS Bull.* **2008**, *33*, 653.

(5) Capelli, R.; Dinelli, F.; Toffanin, S.; Todescato, F.; Murgia, M.; Muccini, M.; Facchetti, A.; Marks, T. J. *J. Phys. Chem C* **2008**, *112*, 12993.

(6) (a) Yoon, M. H.; Kim, C.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 1251. (b) Chua, L.-L.; Zaumseil, J.; Chang, J.-F.; Ou, E. C.-W.; Ho, P. K.-H.; Sirringhaus, H.; Friend, R. H. *Nature* **2005**, *434*, 194.

(7) Bao, Z. A.; Lovinger, A. J.; Brown, J. *J. Am. Chem. Soc.* **1998**, *120*, 207.

(8) (a) Haddon, R. C.; Perel, A. S.; Morric, R. C.; Palstra, T. T. M.; Hebard, A. F.; Fleming, R. M *Appl. Phys. Lett.* **1995**, *67*, 121. (b) Frankevich, E.; Maruyama, Y.; Ogata, H. *Chem. Phys. Lett.* **1993**, *214*, 39. (c) Kobayashi, S.; Takenobu, T.; Mori, S.; Fujiwara, A.; Iwasa, Y. *Appl. Phys. Lett.* **2003**, *82*, 4581. (d) Lee, T. W.; Byun, Y.; Koo, B. W.; Kang, I. N.; Lyu, Y. Y.; Lee, C. H.; Pu, L.; Lee, S. Y. *Adv. Mater.* **2005**, *17*, 2180.

(9) (a) Facchetti, A.; Mushrush, M.; Yoon, M.-H.; Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 13859. (b) Facchetti, A.; Mushrush, M.; Katz, H. E.; Marks, T. J. *Adv. Mater.* **2003**, *15*, 33. (c) Facchetti, A.; Deng, Y.; Wang, A. C.; Koide, Y.; Sirringhaus, H.; Marks, T. J.; Friend, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 4547.

(10) Sakamoto, Y; Suzuki., T; Kobayashi, M; Gao., Y; Fukai., Y; Inoue., Y; Sato., F; Tokito, S *J. Am. Chem. Soc.* **2004**, *126*, 8183.

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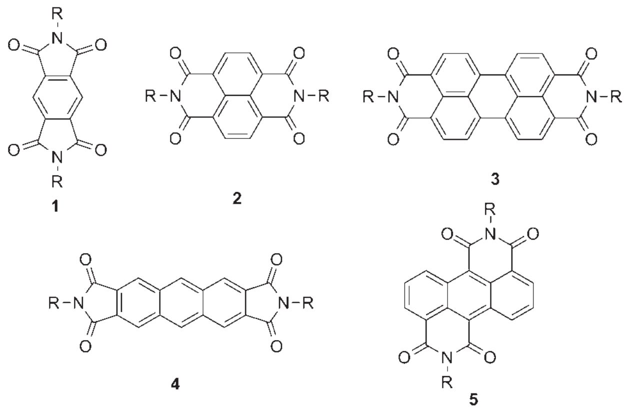


Figure 1. Chemical structure of some diimide molecules.

benzene, naphthalene, perylene, and linear anthracene diimide small molecules (Figure 1) have received attention for their high electron affinities, high electron mobility, excellent thermal and oxidative stability, and finally, robustness vis-à-vis environmental stresses.[12] They are, therefore, promising candidates for a variety of organic electronic applications.

Compared to work on naphthalene and perylene (rylene) diimides,[13] there have been very few reports on benzene and anthracene diimides.[14] Devices based on the latter, bearing the same N-substituents, exhibit mobilities an order of magnitude lower than the naphthalene and perylene analogues.[11d] This result is probably related to their structural difference, possibly five- vs six-membered imide rings (Figure 1).

Herein, we report the synthesis of a new monomer for polyimides as well as an electron-deficient semiconductor based on the previously unknown anthracene-1,9:5,10-tetracarboxylic diimide containing six-membered imide rings **5a**–**d**. We also report ab initio molecular orbital calculations of electron distribution in anthracene diimides of **4** and **5**.

The design of molecules **5** was based on a relatively simple valence bond view of the anthracene nucleus, particularly in comparing **4** with **5**. This is easiest seen when comparing the structures upon the addition of an electron and the subsequent stabilization of the radical anion, as shown in Figure 2.

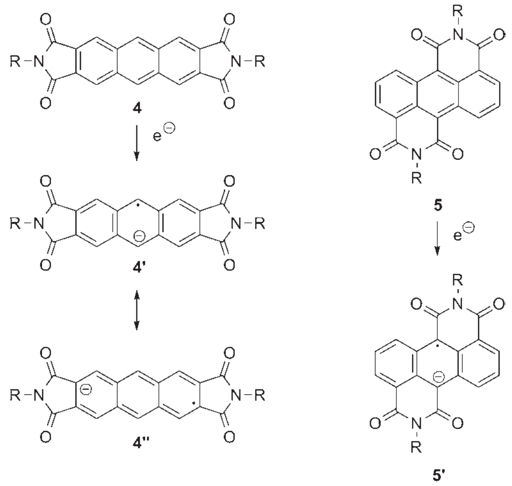
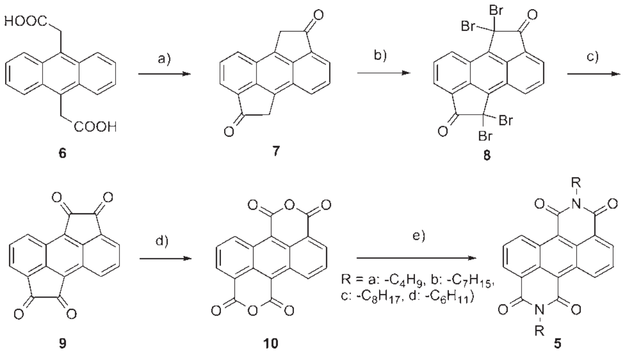


Figure 2. Rational for the design of **5**. In **4** the radical anion cannot be stabilized without disturbing the aromatic sextets (**4″**).

Figure 2 shows that even though in both cases one gains an aromatic sextet upon addition of an electron to **4** and **5**, providing a driving force for this process. However, whereas in **5** the spin and charge find themselves adjacent to a carbonyl for further stabilization by delocalization (**5′**), in **4** two aromatic sextets need to be sacrificed for the equivalent stabilization (**4″**). This concept was verified by electrochemical results (vide infra). In fact, **5** is a slightly stronger acceptor than **3** and a much stronger acceptor than **4**.

Scheme 1 outlines the synthetic route for compound **5**. The synthesis started with acid chloride formation, followed by intramolecular Friedel–Crafts cyclization reaction of 9,10-bis(carboxymethyl)anthracene **6** to produce **7**

Scheme 1. Synthesis of Anthracene Diimides **5a**–**c**. [a]



[a] Reagents and conditions: (a) (i) $SOCl_2$, 80 °C, (ii) $AlCl_3$, $ClCH_2CH_2Cl$; (b) PBr_5, chlorobenzene; (c) DMSO, 100 °C; (d) Oxone, acetic acid; (e) *n*-alkylamine, 80 °C.

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(11) (a) Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Siegrist, T.; Li, W.; Lin, Y. Y.; Dodabalapur, A. *Nature* **2000**, *404*, 478. (b) Chesterfield, R. J.; McKeen, J.; Newman, C. R.; Frisbie, C. D. *J. Appl. Phys.* **2004**, *95*, 6396. (c) Jones, B. A.; Ahrens, M. J.; Yoon, M.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6363. (d) Zhan, X.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R.; Marder, S. R *Adv. Mater.* **2011**, *23*, 268.

(12) Joes, B. A.; Facchetti, A.; Wasielewski, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 15259.

(13) (a) Jones, B. A.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. *Chem. Mater.* **2007**, *19*, 2703. (b) Katz, H. E.; Johnson, J.; Lovinger, A. J.; Li, W. *J. Am. Chem. Soc.* **2000**, *122*, 7787. (c) Chen, H. Z.; Ling, M. M.; Mo, X.; Shi, M. M.; Wang, M.; Bao, Z. *Chem. Mater.* **2007**, *19*, 816. (d) Ling, M. M.; Erk, P.; Gomez, M.; Koenemann, M.; Locklin, J.; Bao, Z. *Adv. Mater.* **2007**, *19*, 1123. (e) Oh, J. H.; Lee, W.-Y.; Torsten, N.; Chen, W.-C.; Könemann, M.; Bao, Z. *J. Am. Chem. Soc.* **2011**, *133*, 4204.

(14) (a) Zheng, Q.; Huang, J.; Sarjeant, A.; Katz, H. E. *J. Am. Chem. Soc.* **2008**, *130*, 14410. (b) Wang, Z.; Kim, C.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 13362.

in an overall yield of 70%.[15] Without any purification, compound **7** was brominated to obtain **8**. A suitable single crystal of **8** was obtained by slow evaporation from solution in dichloromethane (Supporting Information, Figure 5-1).

A solvolytic reaction of **8** in DMSO resulted in bisaceanthrylene-1,2-dione **9**,[16] which was subsequently oxidized to the carboxylic acid anhydride **10** by Oxone.[17] Anhydride **10** is highly fluorescent in solution (Supporting Information, Section.3).

Anhydride **10** can be used as a starting material for the general preparation of **5** by condensation with primary amines. The heptyl, octyl, and cyclohexyl drivatives **5b**–**d** were prepared from **10** and pure amines. The butyl derivative **5a** was obtained from **10** and the corresponding amine in the presence of toluene as solvent.[17] The structures and purities of **5a**–**d** were verified by ^{1}HNMR, ^{13}C NMR, and high-resolution mass spectroscopy (Supporting Information, section 2).

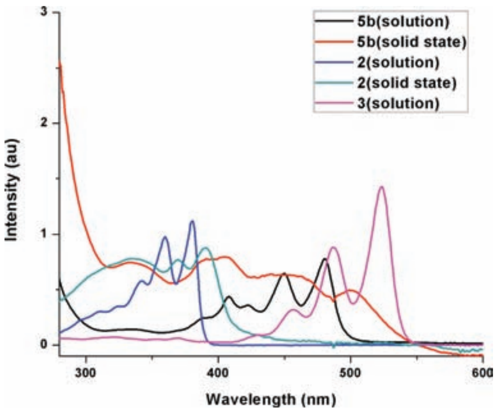

Figure 3. UV/vis absorption spectra of compounds **3** (blue), **5b** (black), and **2** (red) in the solid state and in CH_2Cl_2 as solvent.

Figure 3 shows the optical absorption of anthracene diimide (**5b**), perylene diimide (**3**), and naphthalene diimide (**2**), the latter two for comparison. The solution UV/vis spectrum of **5b** shows an optical absorption centered around 480 nm. This absorption is red-shifted by approximately 100 nm relative to **2** and blue-shifted by approximately 50 nm relative to **3**. Therefore, optical spectroscopy of **5** shows a band gap of ~2.2 eV, reflecting a π–π* gap approximately the same as **3** (~2.2 eV) , but smaller than **4** (~2.6 eV)[14b] and **2** (~2.9 eV).

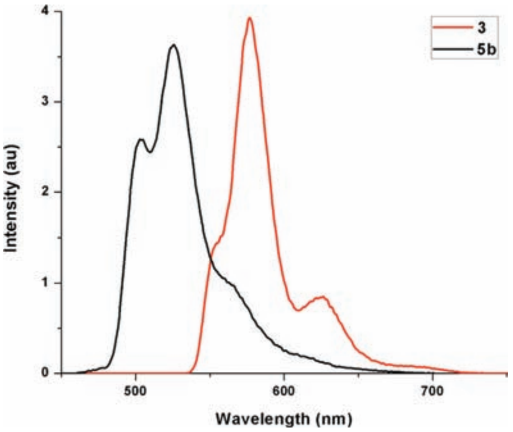

Figure 4. Fluorescence spectra of compounds **3** (red) and **5b** (black) in CH_2Cl_2 as solvent.

Fluorescence spectra of **3** and **5b** are exhibited in Figure 4. Both compounds show high fluorescence in solution with a maximum at 525 and 575 nm, corresponding to a Stokes shift of 45 and 50 nm, respectively. Compound **5b** exhibits a fluorescence quantum yield of 71% in solution.

The electronic properties of the new anthracene dicarboximides **5a**–**c** were examined by cyclic voltametry (Figure 5). The electrochemical reduction potential of the first wave in chlorobenzene vs SCE is −0.22 V for anthracene diimide **5b**, slightly less negative than those of naphthalene and perylene diimides **2** (−0.27 V) and **3** (−0.33 V), respectively, but much less negative than anthracene diimide **4** (−1.1 V).[14b] The two outstanding features are that **5b**, relative to **3** and **4**, has two well-separated, fully reversible processes. The LUMO energy level of **5b** is slightly lower than those of **2** and **3** but much lower than that of **4**. They are, therefore, promising candidates for an air-stable n-channel semiconductor.

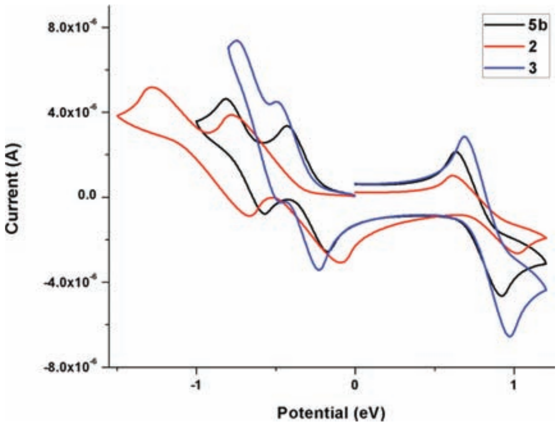

Figure 5. Cyclic voltammograms of **2**, **3**, and **5b** in chlorobenzene, 0.1 M $TBBF_4$. Scan rate = 100 mV/s. Platinum as working electrode, wave at ca. 0.7 eV is the internal Fc/Fc+ reference.

Density functional theory (DFT) calculations were performed at the B3LYP level of theory with a 6-31G* basis

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(15) (a) Amin, S.; Balanikas, G.; Hiie, K.; Hussain, N.; Geddie, J. E.; Hecht, S. S. *J. Org. Chem.* **1985**, *50*, 4642. (b) Ryu, D.; Park, E.; Kim, D. S.; Yan, S.; Lee, J. Y.; Chang, B. Y.; Ahn, K. H. *J. Am. Chem. Soc.* **2008**, *130*, 2394.

(16) Tatugi, J.; Okumura, S.; Izawa, Y. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3311.

(17) Yao, J. H.; Chi, C.; Wu, J.; Loh, K. P. *Chem.—Eur. J.* **2009**, *15*, 9299.

Table 1. Optical and Electrochemical Data

		theoretical data		experimental data		
entry	λ^a (nm)	HOMO (eV)	LUMO (eV)	HOMO (eV)	LUMO^b (eV)	$E_g{}^c$ (eV)
2	430			−6.55	−3.65	2.90
3	545			−5.97	−3.70	2.27
4	475	−6.30	−2.82	−5.76	−3.15	2.61
5b	560	−6.33	−3.51	−6.00	−3.80	2.20

[a] The intercept of the slope of the absorption tail and the minimum absorption. [b] Calculated by measuring the difference between the onset of reduction and the half-wave potential of the ferrocene standard. [c] Calculated from λ_{onset}.

set using the Gaussian 03[18] program. The calculated orbital energies and the tendency of decreasing LUMO energy from 5-membered diimide to 6-membered diimide are in good agreement with the experimentally obtained results (see Table 1). In fact, the DFT calculation shows that the amine nitrogen in the 6-membered rings, in contrast to 5-membered rings, is directly involved in efficient delocalization of electrons with the anthracene backbone, thus increasing the effective conjugation length and resulting in a low-lying LUMO energy level and excellent oxidative stability (Figure 6).

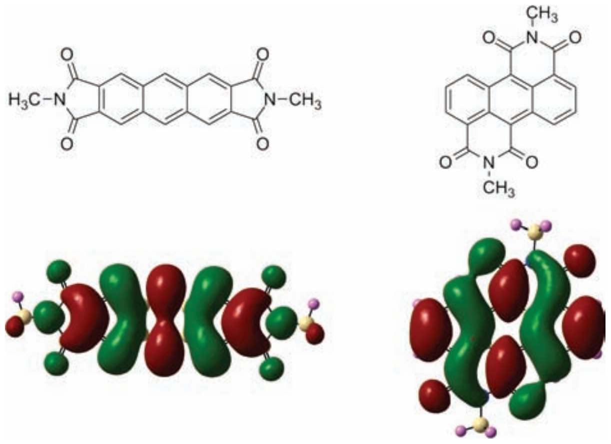

Figure 6. Anthracene rylene diimide structures and lowest unoccupied molecular orbital (LUMO) distribution.

A single crystal of **5a** was obtained relatively easily by slow evaporation from solution in dichloromethane (Figure 7). The molecular structure shows a nearly planar core (dihedral angle of ~4° defined by the planes of anthracene and 6-membered imide rings). The crystal structure is a slip-stacked face-to-face molecular packing with a minimum interplanar spacing of 3.45 Å. This motif and the planar core augurs well for efficient charge-transport properties.

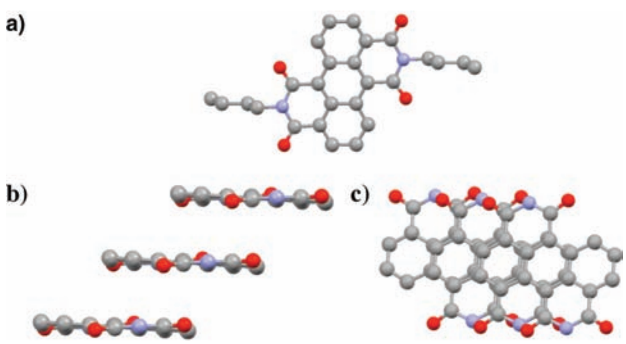

Figure 7. Crystallographic order of compound **5a**: (a) single-molecule; (b) and (c) viewed along two different crystallographic directions. N,N′ groups have been removed for clarity.

In summary, we designed and synthesized new electron-accepting molecules based on a previously unknown anthracene diimide containing six-membered imide rings. The precursor to the imides, the bis anhydride,[19] is a new monomer for polyimides. Compared to a previously reported anthracene diimide containing five-membered imide rings **4**,[13b] our new anthracene diimides **5a**–**d** exhibit better electron-accepting properties with potential application in organic electronics. The theoretical data explain very well the electronic difference in molecular structure of **5** and **4** and also are in good agreement with experimental data.

Acknowledgment. This work was supported by Konarka Technologies Inc. and Department of Energy (Grant No. DE-FG02-08ER46535). Technical assistance from Dr. Guang Wu for the crystal structure is acknowledged.

Supporting Information Available. Spectroscopic and other data for compounds **7**–**10** and **5a**–**d** and crystallographic data for compounds **5a** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Gaussian 03, Revision B.04: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, N.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Zakrzewski, K.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, 2003.

(19) Kinoshita, A.; Suzuki, T.; Sakimura, T. *Jpn. Kokai Tokkyo Koho*, JP 05333574 A19931217, 1993.