The above azido ester was hydrogenated over 150 mg of 5% rhodium-on-carbon catalyst in 25 mL of methanol. The catalyst was filtered and the filtrate concentrated. The residue was crystallized from acetone affording 475 mg (65%) of diketopiperazine **19**: IR (KBr) 3230, 1665, 1650, 1425, 1335, 1060 cm^{-1}; NMR ($CDCl_3$) δ 1.40–2.55 (m, 4 H, $CHCH_2CH_2$), 3.95–4.25 (m, 3 H, OCH_2 and CH), 4.06 (bs, 2 H, CH_2NH), 6.25 (bs, 1 H, NH).

Anal. Calcd for $C_7H_{10}N_2O_3$: C, 49.41; H, 5.93; N, 16.46. Found: C, 49.27; H, 6.06; N, 16.59.

Acknowledgments. The authors are indebted to the National Institutes of Health for its generous support (NIH Grant No. 5R01 GM04229-24, to R.B.W., and Research Fellowship NIH Grant No. 1F32 CA05526-01, to V.J.L.).

Registry No. 2, 38636-09-8; **3**, 36652-42-3; **4**, 70235-93-7; **5**, 70235-94-8; **6**, 70235-95-9; **7**, 70235-96-0; **8**, 70235-97-1; **9**, 70235-98-2; **10**, 70235-99-3; **11**, 70236-00-9; **12**, 70236-01-0; **13**, 70236-02-1; **14**, 70236-03-2; **15**, 70236-04-3; **16**, 70236-05-4; **17**, 70236-06-5; **18**, 70236-07-6; **19**, 70236-08-7; *tert*-butylhydroxylamine, 16649-50-6; chloroacetaldehyde, 107-20-0; *N*-(2-chloroethylidene)-*tert*-butylamine *N*-oxide, 37898-43-4; diethyl(3-chloropropyl)malonate, 18719-43-2; ethyl nitrite, 109-95-5; isoamyl nitrite, 110-46-3; chloroacetyl chloride, 79-04-9; acetyl chloride, 75-36-5; oxalyl chloride, 79-37-8; methyl DL-2-iodoacetyltetrahydro-2*H*-1,2-oxazine-3-carboxylate, 70236-09-8; methyl DL-2-azidoacetyltetrahydro-2*H*-1,2-oxazine-3-carboxylate, 70236-10-1; methylamine, 74-89-5.

3,4:3',4'-Bibenzo[*b*]thiophene

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Received January 8, 1979

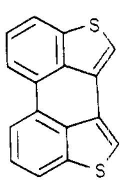
The title compound, isoelectronic with perylene, was prepared in a two-step synthesis. It forms an iodine complex with very similar properties to the known perylene–iodine solids, including electrical conductivity.

One of the first donor–acceptor complexes which exhibited relatively high room-temperature electrical conductivity was a perylene–iodine complex prepared by Akamatu et al., nearly a quarter century ago.[2] Yet it was not until this year that a good single-crystal measurement on the high conductivity of a perylene–iodine complex was performed successfully.[3]

The unusual properties of perylene have been of interest to chemists for some time. Considering its small number of carbon atoms, it exhibits an unusually low ionization potential (IP 7.72 eV) and also an unusually high electron affinity (EA 0.956 eV)![4]

Given these exceptional properties, we decided to determine if replacement of two of the carbon–carbon bonds of perylene by a polarizable element containing a lone pair of electrons (e.g., S, Se, Te) would depress the IP even more and perhaps lead to more stable charge-transfer salts with iodine than those produced by perylene with the same acceptor.[5]

Thus, as a first target we considered the title compound (**1**). Although isomers **2**–**4** would be equally (if not more) interesting heterocyclic analogues of perylene, from a preparative point of view, **1** (BBT) was the simplest to synthesize. We also anticipated that **3** and **4** might actually be unstable at room temperature since they are homologues of isobenzothiophene, a notably unstable compound.[6]



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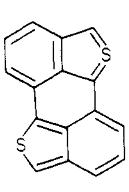

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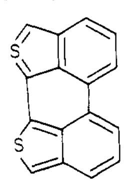
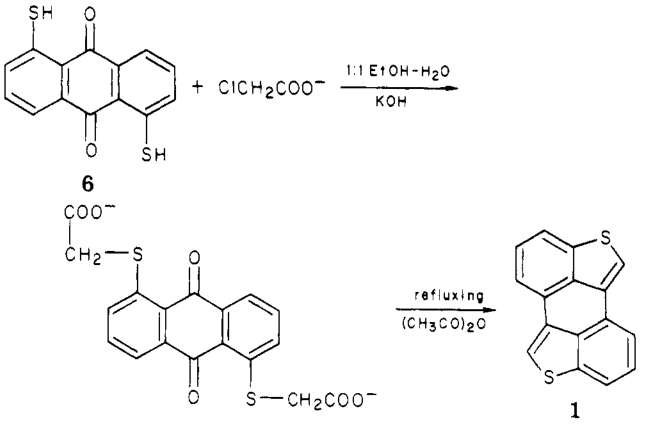
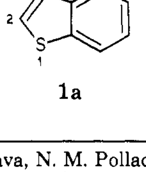


4

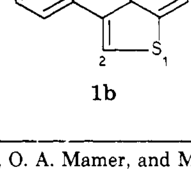
Scheme I



Isomers **1** and **2** can be envisioned as either bibenzothiophenes or derivatives of *p*- and *o*-dibenzoxylylenes, respectively. If one considers the former point of view, compound **1** should exhibit the properties of a perturbed benzo[*b*]thiophene. On the other hand, if one adopts the latter view, positions 2 and 7 should be extremely reactive compared to the reactivity of the same positions in benzo[*b*]thiophene.



1a



1b

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[1] Visiting scientist from the Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N.Y. 11210

[2] H. Akamatu, Y. Matsunaga, and H. Kuroda, *Bull. Chem. Soc. Jpn.*, **29**, 213 (1956).

[3] M. M. Labes (private communication, July 1978) has discovered that perylene–tetrakis(diiodine) is metallic in its conductivity between 340 and 235 K. Many groups have attempted single-crystal measurements of the conductivity; see, for example, J. Kommandeur and F. R. Hall, *J. Chem. Phys.*, 34, 129 (1961).

[4] V. D. Parker, *J. Am. Chem. Soc.*, **98**, 98 (1976).

[5] The perylene–iodine complexes are quite unstable at room temperature and atmospheric pressure and tend to lose iodine readily (J. Kommandeur, see ref 3 above).

[6] M. P. Cava, N. M. Pollack, O. A. Mamer, and M. J. Mitchell, *J. Org. Chem.*, **36**, 3932 (1971).

0022-3263/79/1944-2491$01.00/0

Table I. Absorption Spectra in Ethanol

λ, nm (ε)		
perylene	1	Δ[a]
434 (36 308)[b]	383 (35 540)[b]	−51
406 (26 303)	363 (25 700)	−43
387 (12 023)	346 (11 880)	−41
368 (4786)	330 (4700)	−38
251 (50 119)[c]	252 (38 870)[c]	+1
	244 (30 750)	

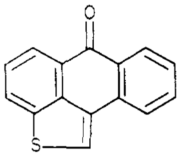
[a] λ(perylene) − λ(1). [b] Second largest absorption (emission). [c] λ_{max}.

Table II. Fluorescence Spectra

λ, nm (ε)		
perylene	1	Δ[a]
535	465	−70
495	435	−60
467[b]	442[b]	−25
440[c]	392[c]	−48

[a] λ(perylene) − λ(1). [b] Second largest absorption (emission). [c] λ_{max}.

Synthesis. To the best of our knowledge, the title compound has not been described in the chemical literature. Compound 5 was prepared by Gattermann in 1912.[7]



5

This material made the synthetic scheme (outlined in Scheme I) very facile.

The conversion of 6 to 1 could be carried out with ease in 43% yield. Slight modification of this scheme could produce the selenium analogue.

Physical and Chemical Properties. The title compound crystallizes in yellow, thin, transparent flakes (mp 295–296 °C (sublimation)) from carbon disulfide. It is sparingly soluble in most organic solvents, practically insoluble in methanol, and soluble in warm carbon disulfide and in concentrated sulfuric acid with formation of a deeply colored (emerald green) solution. A trace of radical cation could be detected via ESR in this solution.

Examination of Tables I and II reveals that there are surprising hypsochromic shifts in the UV–visible region and the fluorescence spectra of 1 relative to perylene, whereas comparisons within Table III show (with the exception of one band) that benzo[*b*]thiophene exhibits bathochromic shifts relative to naphthalene.

Electrochemistry in acetonitrile revealed an oxidation wave at 1.03 V vs. SCE. This value indicates that 1 is slightly easier to oxidize than perylene ($E_{1/2}$ = 1.06 V, CH_3CN vs. SCE).[4] From this value we predicted that chlorine or bromine would oxidize 1 to the radical cation. In fact, both reagents produced only covalent derivatives whose structures are under investigation.

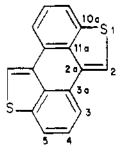
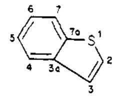
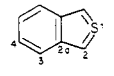
To examine the possibility that the radical cation was too electrophilic for the relatively nucleophilic chloride and bromide counterions, we tested a nonnucleophilic oxidizing agent. Thus a dichloroethane solution of a hexafluoroantimonate produced by addition of antimony pentafluoride to 1 gave rise to a clean ESR spectrum. The coupling constants derived from such a spectrum together with calculated values for 1 and other comparable materials are recorded in Table IV.

Table III. Absorption Spectra

λ, nm (ε)		
naphthalene	benzo[*b*]thiophene	Δ[a]
286 (3760)	297 (2870)	+11
283 (3710)	288 (2030)	+5
275 (5530)[b]	256 (5420)[b]	−19
266 (4990)		
258 (3470)		
221 (10 600)[c]	226 (27 900)[c]	+5

[a] λ(naphthalene) − λ(benzo[*b*]thiophene). [b] Second largest absorption. [c] λ_{max}.

Table IV. Spectral Parameters and Calculated Spin Densities

			hfs	
molecule	atom	ρ_s^{π}-(calcd)[a,b]	exptl	calcd[b]
	C_4	0.007	0.18	0.20
	C_3	0.050	1.36	1.65
	C_{3a}	0.040		
	C_{2a}	0.059		
	C_{11a}	0.000		
	C_{10a}	−0.015		
	C_5	0.081	2.19	2.90
	C_2	0.180	4.87	4.20
	S_1	0.098	3.007	3.226
	C_{7a}	0.003		
	C_7	0.086		2.32
	C_6	0.120		3.26
	C_5	−0.030		0.82
	C_4	0.202		5.46
	C_{3a}	−0.035		
	C_3	0.294		7.93
	C_2	0.089		2.40
	S_1	0.272		8.98
	C_{2a}	−0.031		
	C_3	0.133		3.58
	C_4	0.042		1.15
	C_2	0.397		10.73
	S_1	−0.082		2.22

[a] Calculated spin density. [b] F. B. Bramwell, R. C. Haddon, F. Wudl, M. L. Kaplan, and J. H. Marshall, *J. Am. Chem. Soc.*, **100**, 4612 (1978).

Treatment of 1 with iodine in either chloroform or chlorobenzene, but not in carbon disulfide or acetonitrile, produced a charge-transfer complex which separated as fine, shiny black needles. Upon storage of this product in a closed vial overnight at room temperature, molecular iodine appeared on the cap, indicating that this complex is as weak as perylene iodine (in accord with the similarity in the oxidation potentials of 1 and perylene).

Results and Discussion

It is clear from the above observations, particularly ESR spectroscopy and calculations compiled in Table IV, that the title compound should be considered more akin to a dibenzoxylylene (**1b**) than **1a**. Also, substitution of two sulfurs for two double bonds in perylene has had no beneficial effect on the stability of the resulting iodine complex. This perturbation of perylene has also had practically no effect on the room-temperature compressed-pellet resistivity of the iodine complex (ρ(perylene)[8] = 2–125 Ω cm; ρ(1) = 5–40 Ω cm).

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(7) L. Gattermann, *Justus Liebigs Ann. Chem.*, **393**, 113 (1912).

(8) F. Gutmann and L. E. Lyons, "Organic Semiconductors", Wiley, New York, 1967, Table 8.5, pp 725–726, and references within.

To this day it is not known with certainty why the perylene–iodine complexes, or in this case the BBT (1)–iodine complexes, conduct electricity. Since both perylene–bromine and –iodine complexes are good conductors, one can probably rule out conductivity by the halogen because there are no known polybromides which are conductors. Also, all well-known organic conductors exhibit a high degree of transport along segregated, partially charged stacks of donors and/or acceptors.[9] On the other hand, iodine clathrates (presumably containing iodine chains)[10] exhibit some conductivity (ρ on the order of 10^4–10^5 Ω cm),[11] but these resisitivity values are much higher than the low resistivity exhibited by the above complexes. It is possible that the conductivity in the above complexes is due to a combination of effects: iodine chains and stacked, partially charged donors. The final proof has to rest with an X-ray structure determination. This is quite imperative, since there is no reliable X-ray structure available for $\mathrm{Per}_x\mathrm{I}_y$.[12-14] Large single crystals of $(\mathrm{BBT})\mathrm{I}_3$ suitable for a solid-state structure determination were grown from chloroform solution[16] and their solid-state structure is currently under investigation.

In conclusion, and contrary to expectations, BBT is virtually identical with perylene with the exception of a hypsochromic shift in its electronic absorption and emission spectra and a higher reactivity toward electrophilic substitution.

Experimental Section

Preparation of 3,4:3′,4′-Bibenzothiophene (1). A solution of anthraquinone 1,5-dithiolate was prepared by the procedure developed by Jenny[15] for the preparation of the 1,4 isomer. To this solution was added an excess of chloroacetic acid. The mixture was heated to reflux for ca. 2 h, filtered, cooled, acidified with hydrochloric acid, and centrifuged (the precipitated, crude diacid was found to be virtually impossible to filter). The muddy, green residue was washed with water, ethanol, and ether and allowed to dry. Since it was virtually insoluble in all common organic solvents, it was not purified further but was used directly in the next step.

A suspension of 5.7 g of the above diacid in 228 mL of anhydride was heated to reflux (bath temperature ca. 168 °C). A fine stream of gas evolved. After 1.5 h of refluxing, the mixture was filtered hot. As the filtrate cooled, yellowish crystals separated. The crude crystals were chromatographed on 40 mL of $\mathrm{Al_2O_3}$ (Woelm grade I) with carbon disulfide as eluent. The first band contained pure 1 as yellow platelets: 1.67 g; 43% yield; mp 294.6–295.9 °C subl; mass spectrum m/e 264 (P), 132 (base peak); NMR ($\mathrm{CS_2}$) δ 7.0–7.5, m.

Iodine Complex. Attempts to grow an iodine complex from chloroform solution by slow diffusion in an inverted U-tube failed. Slow cooling of a chlorobenzene solution afforded small, black lustrous needles. The supernatant solution was decanted and the solid was washed four times with a small amount of hexane to remove residual chlorobenzene. The hexane washings were always slightly purple, indicating that some iodine was being washed away with the residual chlorobenzene. The solid was then dried under a fast stream of nitrogen and analyzed. As expected,[3] BBT forms more than one phase in its reaction with iodine. So far, the compounds $(\mathrm{BBT})\mathrm{I}_{2.4}$ and $(\mathrm{BBT})\mathrm{I}_3$[16] have been isolated. Several elemental analyses of the $(\mathrm{BBT})\mathrm{I}_{2.4}$ phase gave average values: C, 33.67; H, 1.15; I, 53.50; S, 11.19. These correspond to $(\mathrm{BBT})\mathrm{I}_{2.4\pm0.2}$ (calcd for $\mathrm{C_{16}H_8I_{2.4}S_2}$: C, 33.75; H, 1.40; I, 53.58; S, 11.25). While the analysis agreement for this nonstoichiometric formulation is excellent, we know it cannot correspond to the highly conducting complex because we found that room-temperature conductivity decreased with increasing hexane washings (decreasing $\mathrm{I_2}$ content).[17] More careful in-house analyses of $(\mathrm{BBT})\mathrm{I}_{2.4}$ gave the same results, indicating that conventional microanalytical techniques are not sensitive enough to detect the minor changes in stoichiometry which give rise to noticeable changes in conductivity.

A small sample of $(\mathrm{BBT})\mathrm{I}_{2.4}$ was placed in a vacuum oven (~100 torr) at ca. 40 °C for ca. 48 h. When the yellowish brown residue was suspended in methylene chloride, the solvent became slightly purple-brown and the solid became bright yellow. The melting point of this yellow, crystalline residue indicated it was unchanged BBT.

Acknowledgments. We thank D. J. Freed for mass spectral and fluorescence spectroscopy, M. L. Kaplan for electronic spectroscopy, and J. H. Marshall for ESR spectroscopy.

Registry No. 1, 70160-67-7; 6, 70160-68-8; 6 S,S-diacetic acid, 70160-69-9; naphthalene, 91-20-3; benzo[b]thiophene, 95-15-8; benzo[c]thiophene, 270-82-6; perylene, 198-55-0; chloroacetic acid, 79-11-8; 1 iodine complex, 70160-70-2.

(9) H. J. Keller, Ed., "Chemistry and Physics of One Dimensional Metals", NATO Advanced Study Institutes Series, Plenum Press, New York, 1977.

(10) However, see R. C. Teitelbaum, S. L. Ruby, and T. J. Marks, *J. Am. Chem. Soc.*, **100**, 3215 (1978), for reinterpretation in terms of $\mathrm{I_5^-}$.

(11) M. M. Labes, *Org. Solid State, Proc. Int. Symp., 5th.* (1978).

(12) The X-ray structure analysis on perylene–iodine complexes as performed by Uchida[13] is quite confusing and most probably wrong since there is evidence from Raman spectroscopy that there are $\mathrm{I_5^-}$ units in perylene–iodine.[14]

(13) T. Uchida and H. Akamatu, *Bull. Chem. Soc. Jpn.*, **34**, 1015 (1961).

(14) T. J. Marks, private communication, July 1978.

(15) W. Jenny, *Helv. Chim. Acta*, 41, 317 (1958).

(16) M. M. Labes and H. I. Kao, private communication.

(17) The same behavior was observed with perylene iodine.[3]

Thione S-Imides. Reaction with the Carbon–Carbon Double Bond: 1,3-Dipolar and Diels–Alder-Type Cycloaddition and Ene Reactions

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Thione S-imide (1) reacted as a 1,3 dipole with enamine (5), vinyl ethers (2), bicyclo olefins (10, 12), and cyclopentadiene (18) to give 1,3 dipolar cycloadducts, while with acyclic dienes (14) the imide reacted as a dienophile to give Diels–Alder-type cycloadducts. Furthermore, the imide and (1-cyclohexenyl)amines (7) afforded ene-reaction products.

In our previous work, thione S-imides (1) were readily prepared by a Wittig-type reaction of phosphonium ylides with N-sulfinyl-p-toluenesulfonamide, and some cycloaddition reactions of 1 were described briefly.[1,2] Recently,

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