Synthesis and Reactions of Perylenecarboxylic Acid Derivatives. VI. Sulfonation of 3,4-Perylenedicarboximide

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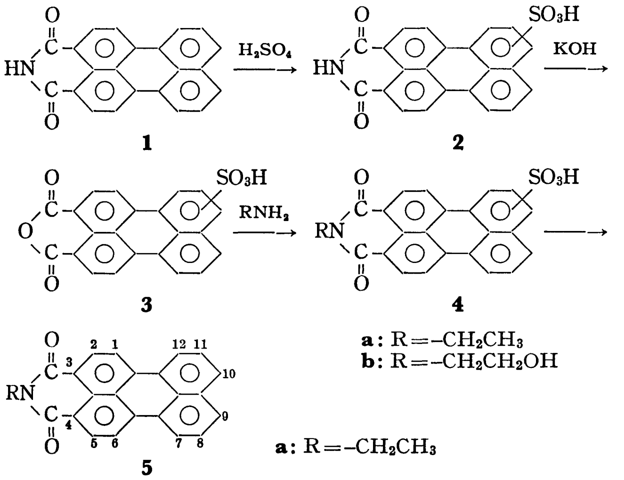
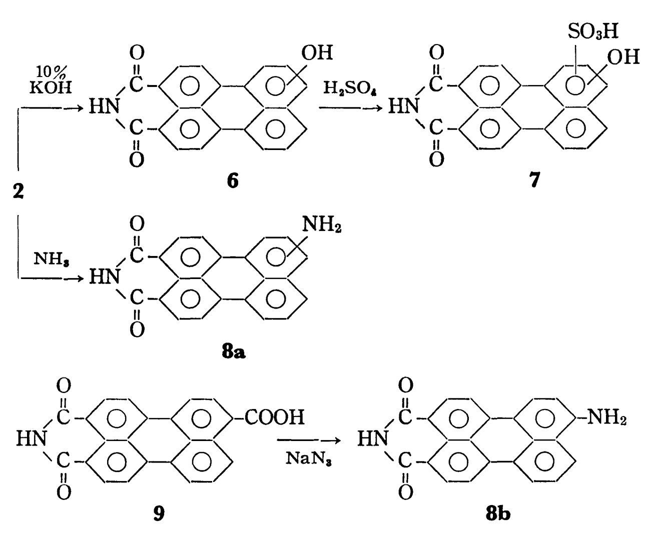
The sulfonation of 3,4-perylenedicarboximide (**1**) with sulfuric acid has been studied. The position of the sulfo group in the monosulfonated product (**2**) obtained at 100 °C has been discussed on the basis of the NMR and IR spectra of **2** and the related compounds, and has been confirmed to be the 9-sulfoperylene-3,4-dicarboximide. The localized treatment of **1** by Hückel and Pople MO calculations confirmed substitution at the 9-position. Paper chromatographic analysis indicated that the reaction product was only **2** in the temperature range 60—120 °C, and the reaction rate was determined spectroscopically. The maximum formation of **2** was approximatedly 97% at 100 °C. The rate of reaction was found to be a pseudo first order process and the activation energy found to be 19.5 kcal/mol.

In a previous publication the 3,4-perylenedicarboximide (PDCI) (**1**) was sulfonated at 100 °C, and the *N*-substituted-perylene-3,4-dicarboximide (*N*-R-PDCI) (**5**) prepared from the sulfonic acid (PDCI-SO_3H) (**2**) *via* **3** and the *N*-substituted-sulfoperylene-3,4-dicarboximide (*N*-R-PDCI-SO_3H) (**4**), as presented below.[1]



The substituted position of the sulfo group in **2**, however, remains. The position of substitution has been discussed on the basis of the NMR and IR spectra data of **2** and related compounds; **4a**, **4b**, **5a**, **7**, **8a**, perylene, perylenedisulfonic acids, and **8b**. The kinetics of the sulfonation of **1** have also been determined.



Experimental

Materials. PDCI (**1**), the potassium salt of PDCI-SO_3H (PDCI-SO_3K), the potassium salt of *N*-(2-hydroxyethyl)-PDCI-SO_3H (**4b**), the potassium salt of *N*-ethyl-PDCI-SO_3H (**4a**), and *N*-ethyl-PDCI (**5a**) were prepared and purified by previous methods.[1] The free sulfonic acid was prepared by adding hydrochloric acid to the solution of the potassium salt. PDCI-SO_3H was confirmed to be a free sulfonic acid by titration with potassium hydroxide solution and in the TG analysis the water of hydration was lost at 100 °C. PDCI-SO_3H dried at 100 °C was used as the standard reagent for spectroscopical determination.

Perylene was prepared from 3,4,9,10-perylenetetracarboxylic dianhydride by the method of Goto *et al.*[2] Perylenedisulfonic acid was prepared by the methods of Marschalk.[3]

Measurements and Molecular Orbital Calculations. The NMR spectra were obtained using a JNM-4H-100 spectrometer (Japan Electron Optics Laboratory Co.) at 100 MHz. All spectra were measured in DMSO-d_6 using TMS as an internal standard and samples for measurement at 150 °C were contained in sealed tubes. Mass spectra were obtained using a Hitachi RMU-7M mass spectrometer. Visible spectra were measured using a Hitachi 124 spectrometer for solutions in concd sulfuric acid and IR spectra on a Nippon Bunko IR-E spectrophotometer. The developing solvent used in paper chromatography was a 1-butanol–pyridine–28 % ammonia–water mixture (1 : 1 : 1 : 1). The molecular orbitals were calculated using an IBM 370 computer with a modification of the program of Wiberg.[4]

Sulfonation of Hydroxyperylene-3,4-dicarboximide. Hydroxyperylene-3,4-dicarboximide (6): In an autoclave was added PDCI-SO_3K 0.60 g and 10% KOH 50 ml. The autoclave was heated at 200 °C for 10 h with stirring. The reaction mixture was filtered, the precipitate washed with water, and poured into water. The suspension was acidified with hydrochloric acid and filtered and the precipitate washed with water, and dried, **6** 0.50 g: λ_{max} (H_2SO_4) 620 nm; R_f 0.78 (violet); MS (70 eV), *m/e* 337 (M^+). After sublimation at 400 °C/3—5 mmHg, an analytical sample was given.

Found: C, 77.53; H, 3.05; N, 4.08%. Calcd for $C_{22}H_{11}O_3N$: C, 78.33; H, 3.29; N, 4.15%.

Sulfonation of Hydroxyperylene-3,4-dicarboximide: Into a three necked flask fitted with a stirrer was added concentrated sulfuric acid 20 ml and **6** 0.10 g. The mixture was warmed at 50 °C for 2 h with stirring, and the cooled mixture poured into ice water 100 ml. The mixture was filtered and the solid dissolved in refluxing ethanol, and filtered to remove the unreacted **6**. The solution was concentrated in an evaporator, and concentrated hydrochloric acid added until the material solidified. The solid was filtered and dried, giving the sulfonic acid **7** 0.08 g: λ_{max} (H_2SO_4) 623 nm; R_f 0.62 (violet).

Aminoperylene-3,4-dicarboximide. *Preparation from PDCI-SO_3K*: In an autoclave was added PDCI-SO_3K 0.50 g and 28% ammonia 50 ml, followed by ammonia gas until a pressure of 10 kg/cm^2 was attained. The autoclave was heated at 200 °C for 10 h. The reaction mixture was filtered, and the precipitate washed with hot 1% potassium hydroxide to remove the unreacted PDCI-SO_3K. The precipitate was washed with water and dried, giving the amine **8a** 0.32 g: λ_{max} (H_2SO_4) 609 nm; R_f 0.88 (blue); MS (70 eV), *m*/*e* 336 (M^+). After sublimation at 400 °C/1 mmHg, an analytical sample was given.

Found: C, 78.23; H, 3.31; N, 7.72%. Calcd for $C_{22}H_{12}N_2O_2$: C, 78.56; H, 3.60; N, 8.33%.

Preparation from 9-Carboxy-3,4-perylenedicarboximide (**9**): **9** 0.50 g was dissolved in concentrated sulfuric acid 25 ml and to the solution was slowly added sodium azide 0.10 g. The solution was maintained at 50 °C for 4 h and then the reaction mixture was poured into water and filtered. The precipitate was washed with hot 1% potassium hydroxide, water, ethanol, and dried, giving the amine **8b** 0.22 g: λ_{max} (H_2SO_4) 609 nm; R_f 0.88 (blue); MS (70 eV), *m*/*e* 336 (M^+). The DMSO solution gave an analytical sample by acidification with hydrochloric acid.

Found: C, 71.08; H, 3.23; N, 6.59 %. Calcd for $C_{22}H_{12}N_2O_2+HCl$: C, 70.88; H, 3.51; N, 7.51%.

Sulfonation of PDCI. In order to study the rate of sulfonation, concentrated sulfuric acid 25 ml was added into a three necked flask, and the temperature of the flask adjusted to the temperature of the rate measured. To the flask was added PDCI 0.50 g and the flask maintained at the same temperature with stirring. An aliquot of the reaction mixture was withdrawn periodically and analyzed by paper chromatography and spectroscopy.

Paper Chromatography: The reaction mixture was poured into water and the precipitated reaction mixture separated by centrifuging. The precipitate was dissolved in 1% potassium hydroxide, placed on the paper and developed by the solvent.

Determination by Spectroscopy: The reaction mixture were diluted with concentrated sulfuric acid, and the absorbance at two wavelength (570 and 585 nm) measured. The mole ratio of PDCI and PDCI-SO_3H to the mixture was calculated from the following relationship:

$$A_{570} = 0.743 \times (\text{PDCI}) + 0.583 \times (\text{PDCI-SO}_3\text{H})$$

$$A_{585} = 0.714 \times (\text{PDCI}) + 0.726 \times (\text{PDCI-SO}_3\text{H})$$

A_{570} and A_{585}; Absorbances of the reaction mixture at 570 and 585 nm. (PDCI) and (PDCI-SO_3H) are the concentrations of PDCI and PDCI-SO_3H (mg/ml), respectively.

Results and Discussion

NMR Spectra of Sulfonic Acids. The sulfonic acid **2** was confirmed to be a mono-sulfonic acid by the potassium analysis of the potassium salt of **2**.[1] The position of the sulfo group in **2** has been evaluated by comparing the NMR spectra of the related compounds, the spectra data being shown in Table 1. Assignment of the proton positions has been assumed on the basis of the perylene spectrum (in CCl_4).[5,6] The differences between the spectra in DMSO-d_6 and CCl_4 were significantly small.

Table 1. NMR spectra of perylene derivatives

Compound	Chemical shift δ/ppm	Position
2[a]	11.5—11.6 (1H, singlet)	N
	8.8—9.1 (1H, doublet)	10
	8.0—8.5 (7H, multiplet)	1, 2, 3, 6, 7, 8, 12
	7.5—7.8 (1H, triplet)	11
4a[a]	8.8—9.1 (1H, doublet)	10
	8.0—8.5 (7H, multiplet)	1, 2, 3, 6, 7, 8, 12
	7.5—7.8 (1H, triplet)	11
4a[b]	9.0—9.2 (1H, doublet)	10
	8.4—8.6 (6H, multiplet)	1, 2, 3, 6, 7, 12
	8.1—8.2 (1H, doublet)	8
	7.5—7.8 (1H, triplet)	11
4b[a]	8.8—9.1 (1H, doublet)	10
	8.0—8.5 (7H, multiplet)	1, 2, 3, 6, 7, 8, 12
	7.5—7.8 (1H, triplet)	11
10[a]	8.3—8.5 (4H, doublet)	X
	7.8—7.9 (4H, doublet)	B
	7.4—7.7 (4H, triplet)	A
11[a]	8.7—8.9 (2H, doublet)	4, 10
	8.3—8.5 (4H, triplet)	1, 6, 7, 12
	7.9—8.1 (2H, doublet)	2, 8
	7.4—7.7 (2H, triplet)	5, 11
5a[b]	8.2—8.6 (6H, multiplet)	1, 2, 5, 6, 7, 12
	7.7—8.0 (2H, doublet)	9, 10
	7.5—7.7 (2H, triplet)	8, 11
7[a]	11.4—11.6 (singlet)	N
	8.0—8.5 (multiplet)	
	7.4—7.9 (triplet)	

a) Measured at 25 °C. b) Measured at 150 °C.

Both **4a** and **4b** exhibited similar peaks to **2** except the peak δ 11.5—11.6 — the addition of D_2O to the solution of **2**, caused the peak at 11.5—11.6 to diminish. The potassium salt showed a similar relation. Thus in the spectrum of **2**, the δ 11.5—11.6 peak has been assigned to the proton of the imide group, and δ 8.8—9.1 and 7.5—7.8 to the single proton in the perylene ring.

The structures of the perylenedisulfonic acids have not been confirmed as 3,9- or 3,10-disulfonic acids, and it is expected that there will be no significant differences in the spectra due to the symmetrical structures. Consequently the structure of the 3,9-derivative (**11**) has been tentatively assigned on the following basis (Table 1): the δ 8.3—8.5 triplet signals appear to overlap the two doublet signals, and the δ 8.7—8.9 signal has been attributed to the 4 and 10 positions, since the steric effect of the sulfo group is larger than that of the others.

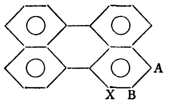
The NMR spectrum of **5a**[†] shows that the imide group does not influence the protons at the 8, 9, 10, and 11 positions.

[†] In order to examine the influence of the imide group the NMR spectrum of **5a** was taken at 150 °C—**5a** has the greatest solubility among the other *N*-substituted PDCI.

TABLE 2. ELECTRON DENSITIES AND THE CHEMICAL SHIFTS OF **5a**

Position	Electron densities		Chemical shifts (ppm)	
	Hückel	Pople	**5a**	Perylene
1, 6	1.007	1.297	8.2—8.6	8.3—8.5
2, 5	0.895	0.596	8.2—8.6	7.4—7.7
7, 12	0.914	0.785	8.2—8.6	8.3—8.5
8, 11	1.001	1.124	7.5—7.7	7.4—7.7
9, 10	0.918	0.826	7.7—8.0	7.8—7.9

The ring proton shift has been found to be approximately proportional to the calculated charge densities on the attached ring-carbon sites.[7] In the polycyclic molecules however, the resonance shifts of a particular ring proton need be corrected for the ring current of the neighbouring rings.[8] There have been several theoretical studies of NMR chemical shifts in polycyclic aromatic hydrocarbons on the basis of the ring current theory.[5,6,9,10] For a complex molecule such as **5a** both the charge densities and ring currents must be considered. The electron densities of **5a** (see later) and the chemical shifts of the protons are shown together with the chemical shifts of perylene in Table 2. The lowest density position showed the largest proton shift to lower field for perylene.



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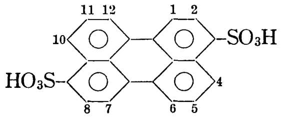

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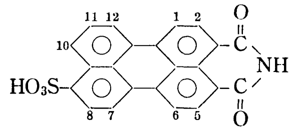


2a

The NMR spectra of **4a** at 150 °C gave sharper peaks than at room temperature. The peaks at δ 9.0—9.2, 8.1—8.2, and 7.5—7.8 almost coincide with the peaks at 8.7—8.9, 7.9—8.1, and 7.4—7.7 of perylenedisulfonic acids. Therefore on the basis of the NMR spectra of the related compounds, **2** has been estimated as the 9-sulfonic acid (**2a**), and the position of the proton assigned as in the Table. Substitution of the sulfo group confirmed that the peak near δ 9.1 was not observed, as shown in the spectrum of **7**.

Preparation of the Amine from the Sulfonic Acid. By the reaction of the sulfonic acid **2** with NH_3, the corresponding amine **8a** has been prepared and compared with the amine **8b**, prepared by the Schmidt reaction from 9-carboxy-3,4-perylenedicarboximide (**9**). These compounds were very difficult to purify due to poor properties of sublimation and solubility in the solvent. Subsequent analysis gave rather low N analysis (%) but the effect of impurities on the spectra as shown in Fig. 1 is negligible since paper chromatography gave only one spot. Both the IR (Fig. 1) and mass spectra of **8a** and **8b** showed the same spectra.

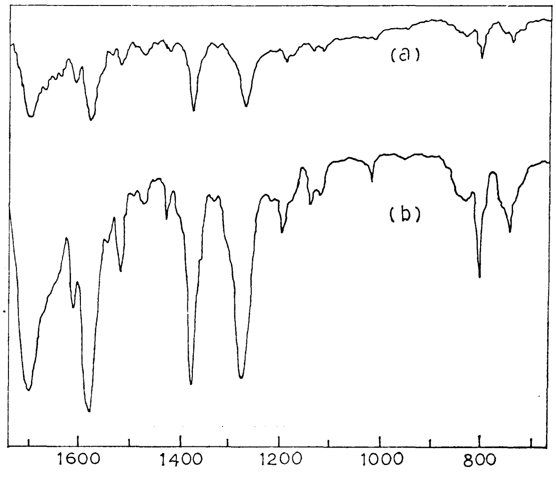
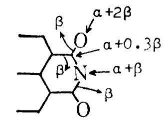


Fig. 1. IR spectra of aminoperylene-3,4-dicarboximide; (a) **8b**, (b) **8a**.

Localized Treatment of the Hückel and Pople Method. The total energies of the calculated models (Fig. 2) for perylene and PDCI by the methods of Hückel[11,14] and Pople[12,13] have been calculated for the localized treatment of electrophilic aromatic substitution.[15,16] The parameters used are shown in Table 3 and the calculated total energies are shown in Table 4. The results show that 9-substitution for PDCI and 3-substitution for perylene have the lowest energy and thus the quantum chemical calculations support the conclusions.

Sulfonation of PDCI. *Yields of Sulfonation*: From paper chromatography, the reaction products were

TABLE 3. PARAMETERS FOR HÜCKEL AND POPLE CALCULATIONS

Hückel[a)]	Pople[b)] (eV)			
		W_{2pi}	(ii,ii)	(ii,jj)
	C^+	-11.16	10.988	$\dfrac{e^2}{\{r_{ij}^2+\frac{1}{4}[(ii,ii)+(jj,jj)]^2\}^{1/2}}$
	N^{2+}	-28.53	16.574	
	O^+	-17.70	13.827	
	$\beta_{C=C}$;	-1.7515		
	β_{C-N};	-1.4030		
	β_{C-O};	-2.220		

a) Ref. 15. b) Ref. 13, W_{2pi}; ionization potentials, (ii,ii) and (jj,jj); one-center repulsion integrals, (ii,jj); two-center repulsion integrals, r_{ij}; distances, β; resonance integrals.

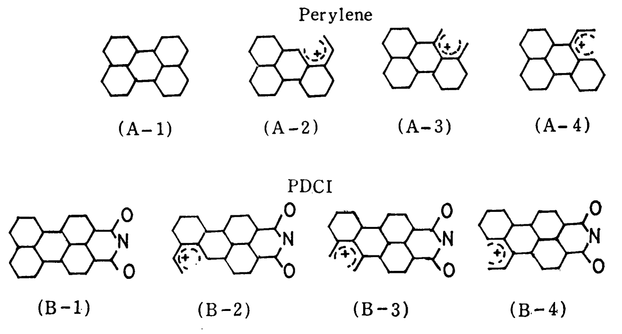


Fig. 2. Calculation models for perylene and PDCI.

Table 4. The total energies of the models

	Perylene			PDCI	
	Hückel $(-\beta)$	Pople (eV)		Hückel $(-\beta)$	Pople (eV)
(A-1)	−28.245	−259.086	(B-1)	−43.042	−369.942
(A-2)	−26.042	−237.604	(B-2)	−40.562	−345.386
(A-3)	−25.735	−235.935	(B-3)	−40.501	−345.470
(A-4)	−26.106	−237.864	(B-4)	−40.654	−345.776

shown to contain only one product **2** until 120 °C, then the reactions were followed spectroscopically. The maximum yield of sulfonic acid was approximately 97% at 100 °C as shown in Fig. 3.

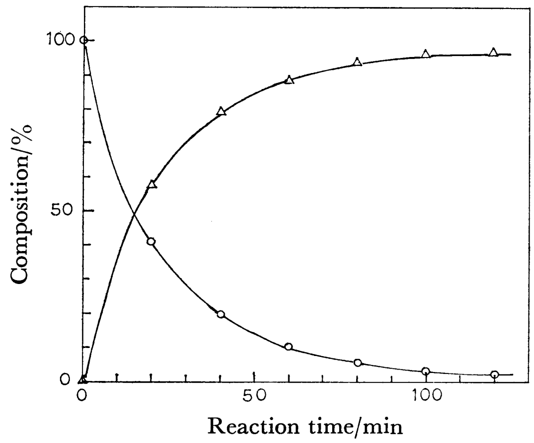


Fig. 3. Sulfonation of PDCI (**1**) at 100 °C. ○; PDCI, △: PDCI-SO$_3$H.

Pseudo First Order Reaction Constant and Activation Energy:

$$\underset{a-x}{\text{PDCI}} \xrightarrow{k} \underset{x}{\text{PDCI-SO}_3\text{H}}$$

The linear plots of $\ln(a-x)/a$ against reaction time t at 63, 80, 100, and 119 °C were obtained at the initial stages in the reaction, where a and x represent the concentrations of initial PDCI and PDCI-SO$_3$H, respectively. The rate constants k, estimated from the slopes have been compared in Table 5. The activation energy was obtained as 19.5 kcal mol^{-1}.

Table 5. Rate constants for sulfonation of PDCI with H$_2$SO$_4$

Temp (°C)	Rate constant k (min^{-1})
119	1.26×10^{-1} [a]
100	3.11×10^{-2} [b]
80	6.74×10^{-3} [a]
63	2.02×10^{-3} [a]

a) Average of two measurements.
b) Average of four measurements.

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