

28. *The Electronic Interaction between Benzenoid Rings in Condensed Aromatic Hydrocarbons. 1 : 12-2 : 3-4 : 5-6 : 7-8 : 9-10 : 11-Hexabenzocoronene, 1 : 2-3 : 4-5 : 6-10 : 11-Tetrabenzoanthanthrene, and 4 : 5-6 : 7-11 : 12-13 : 14-Tetrabenzoperopyrene.*

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Hexabenzocoronene was synthesised from 2 : 3-7 : 8-dibenzoperinaphthene. The unstable perbromide of the dibenzoperinaphthene decomposed when melted and condensed to tetrabenzoperopyrene which was cyclised to hexabenzocoronene. Phenyltribenzoperylene, obtained from dibenzoperylene and phenylacetylene, was cyclised to tetrabenzanthanthrene in a sodium chloride-aluminium chloride melt.

Comparison of the absorption spectra of benzene, triphenylene, 1 : 2-6 : 7-dibenzopyrene, 1 : 12-2 : 3-10 : 11-tribenzoperylene, tetrabenzanthanthrene (VI) and hexabenzocoronene (III) shows the varying degree of electronic interaction between the benzenoid rings * of these hydrocarbons, attributed mainly to contact bonds.

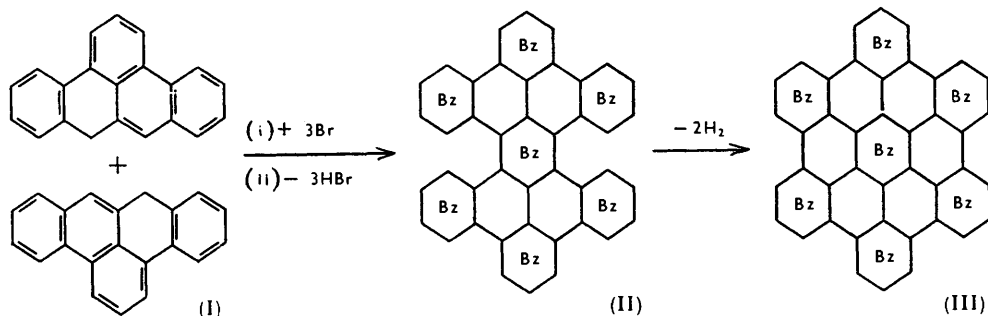
RECENTLY¹ it was shown that the aromatic hydrocarbons triphenylene, dibenzopyrene, tetrabenzanthracene, and tribenzoperylene, containing exclusively benzenoid rings * interlinked by quasi-single bonds, have a very low reactivity. They do not dissolve in concentrated sulphuric acid and show strong phosphorescence of very long life at low temperature. Their absorption bands are shifted more to the violet than are those of the isomeric aromatic hydrocarbons, except for the corresponding polyphenyls with the same number of benzenoid rings; their chemical inertness may be related to this fact.

* In view of the discussion in this paper and to avoid the implication of a particular Kekulé structure, double bonds are omitted from the formulæ unless the discussion requires their inclusion. Bz is used to indicate a ring having benzenoid character, in the sense discussed here and in *J.*, 1958, 1863. No other significance is implied.

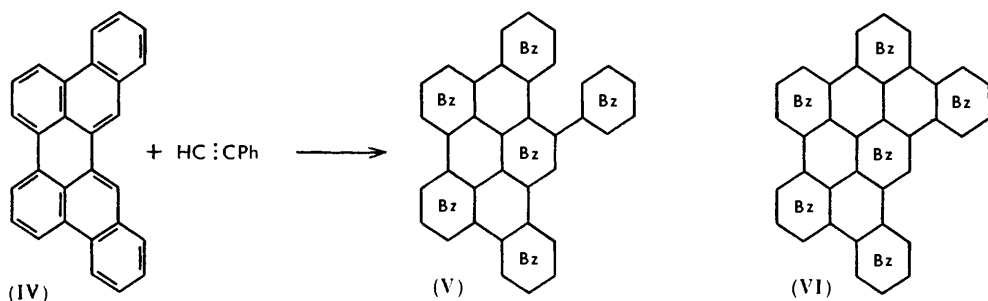
¹ Clar and Zander, *J.*, 1958, 1861.

We have now synthesised another hydrocarbon of this kind, hexabenzocoronene (III), which in addition to these properties has a high degree of symmetry.

2:3-7:8-Dibenzoperinaphthene (I)² in benzene with bromine gave a deep brown perbromide, $C_{21}H_{14}Br_3$, from which the hydrocarbon could be recovered on dissolution in acetone. However, in boiling trichlorobenzene, or when melted, the perbromide gave three molecules of hydrogen bromide and the orange tetrabenzoperopyrene (II). The microwave absorption method showed that the perbromide was not paramagnetic.³ A similar compound, the adduct of one atom of bromine and one molecule of benzanthrone,⁴ also was not paramagnetic.³ This can be explained if the perbromide formed reversibly a crystalline dimer or polymer.



Tetrabenzoperopyrene (II) melted in an evacuated capillary at 482° with evolution of hydrogen, then resolidified and did not melt again below 700°. The extreme stability of hexabenzocoronene, which can be readily sublimed or crystallised from boiling pyrene at about 390°, can be related to formula (III) which contains exclusively benzenoid rings interlinked by quasi-single bonds. This pale yellow hydrocarbon did not dissolve in cold concentrated sulphuric acid and showed an orange-yellow phosphorescence of very long life in solid solution in trichlorobenzene at low temperature, both properties being typical of this kind of hydrocarbon. Hexabenzocoronene (III) can also be obtained by melting dibenzoperinaphthene (I) with sulphur or by sublimation of the distillation residue from the preparation of dibenzoperinaphthene.²



The absorption spectrum of hexabenzocoronene is given in Fig. 1 and that of tetrabenzoperopyrene (II) in Fig. 2. The latter is closely related to that of 4:5-11:12-dibenzoperopyrene;⁵ however, twisting of the molecular plane caused by the four overlapping hydrogen atoms produces a broadening of the *p*-bands. In order to complete the series of hydrocarbons with 1, 2, 3, 4, 5, and 7 benzenoid rings [see (VII)] the missing member with 6 benzenoid rings, 1:2-3:4-5:6-10:11-tetrabenzoanthanthrene (VI) was

² Clar, *Ber.*, 1943, **76**, 611.

³ This investigation was kindly carried out by Mr. P. Carmichael, Department of Natural Philosophy.

⁴ Brass and Clar, *Ber.*, 1936, **69**, 690; Müller and Wiesemann, *Ber.*, 1936, **69**, 2173; Schwab and Schwab-Agallidis, *Z. phys. Chem., B*, 1941, **49**, 196.

⁵ Clar, *Ber.*, 1943, **76**, 458.

synthesised from the dibenzoperylene (IV).¹ The dibenzoperylene with phenylacetylene formed the phenyltribenzoperylene (V), involving similar intermediate stages to those reported in the analogous reaction with maleic anhydride.¹ The spectrum of the hydro-

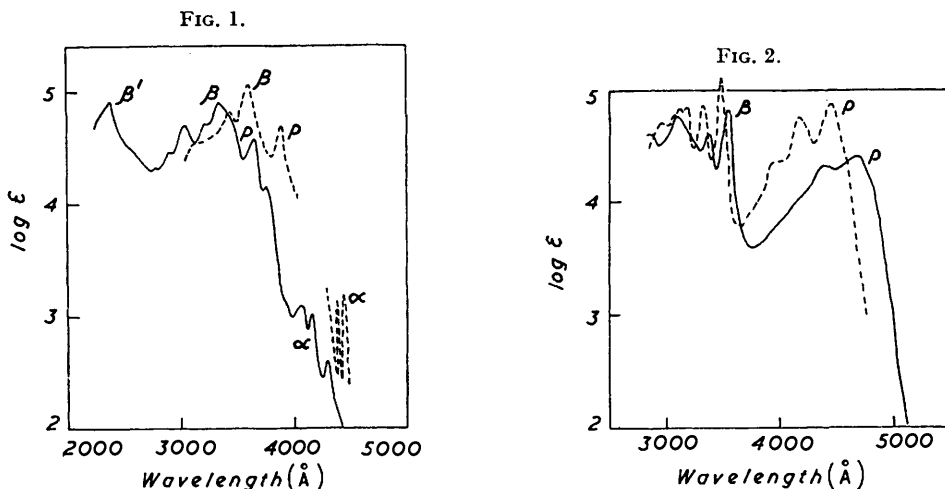


FIG. 1. Absorption max. (Å) and $\log \epsilon$ (in parentheses) of: (—) 1:2-3:4-5:6-10:11-tetrabenzanthanthrene (VI) in trichlorobenzene: α , 4300 (2.60), 4150 (3.01), 4050 (3.09), 3750 (4.15); p , 3650 (4.57); β , 3340 (4.89), 3200 (4.70); in dioxan, 3020 (4.70), 2900 (4.47); β' , 2380 (4.91).

(---) 1:12-2:3-4:5-6:7-8:9-10:11-hexabenzocoronene (III) in trichlorobenzene. Owing to the very low solubility the absolute intensities are uncertain: ($\log \epsilon + X$), p , 3875 (4.68); β , 3600 (5.06), 3425 (4.80). α -Bands were observed visually with a 100-cm. cell, 4440, 4380 (very sharp).

FIG. 2. Absorption max. (Å) and $\log \epsilon$ (in parentheses) of: (—) 4:5-6:7-11:12-13:14-tetrabenzoperylene (II) in benzene; p , 4670 (4.40), 4420 (4.34); β , 3530 (4.83), 3375 (4.61), 3090 (4.78).

(---) 4:5-11:12-dibenzoperylene in benzene; p , 4450 (4.86), 4180 (4.74), 3980 (4.36); β , 3480 (5.10), 3320 (4.85), 3165 (4.83), 3110 (4.83), 2960 (4.70).

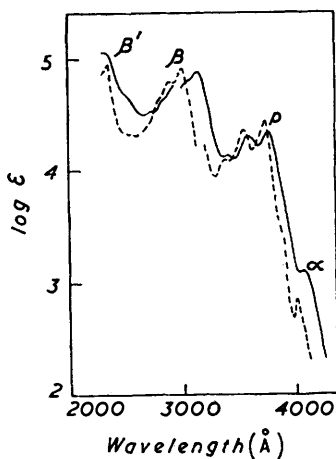


FIG. 3. Absorption max. (Å) and $\log \epsilon$ (in parentheses) of: (—) the phenyltribenzoperylene (V) in trichlorobenzene: α , 4075 (3.12); p , 3775 (4.34), 3580 (4.30), 3400 (4.14); β , 3140 (4.89). From 3000 Å in *n*-heptane; β' , 2340 (5.04).

(---) 1:12-2:3-10:11-tribenzoperylene in trichlorobenzene: α , 4010 (2.86); p , 3740 (4.45), 3540 (4.37), 3380 (4.11); in *n*-heptane, β , 3000 (4.92), 2880 (4.80), β' , 2350 (4.96).

carbon (V) is closely related to that of 1:12-2:3-10:11-tribenzoperylene¹ (Fig. 3); the phenyl ring, being out of plane, has little influence on the absorption spectrum of the non-phenylated compound. The phenyl-compound (V) was cyclised to the tetrabenzanthanthrene (VI) in a sodium chloride-aluminium chloride melt. The pale yellow product showed the expected properties of a purely benzenoid hydrocarbon; it did not dissolve in cold sulphuric acid and showed strong phosphorescence of long life in solid solution in

dioxan at low temperature. The hydrocarbon (VI) (absorption spectrum; Fig. 1) fills the gap in the series between 1 : 12-2 : 3-10 : 11-tribenzoperylene and hexabenzocoronene.

The Table gives a comparison of the spectral changes in passing from benzene to hydrocarbons with 2, 3, 4, 5, 6, and 7 benzenoid rings, as indicated in formula (VII). This comparison is best made with the β -bands; the α -bands, which shift as do the β -bands, are

Hydrocarbon	Number of benzenoid rings	Position				Shift				Ref.
		First β -band		First p -band		First β -band		First p -band		
		\AA	\AA^\ddagger	\AA	\AA^\ddagger	\AA	\AA^\ddagger	\AA	\AA^\ddagger	
Benzene	1	1790V 1819 corr.	42.65	2068A	45.48					<i>a</i>
Diphenyl	2	1980	44.50	2500H	50.00	161	1.85	432	4.52	
Triphenylene	3	2570A	50.70	2840A	53.29	59	6.20	340	3.29	<i>b</i>
Dibenzopyrene	4	2850H	53.39	3257H	57.07	280	2.69	417	3.78	<i>c</i>
Tribenzoperylene	5	3000H	54.77	3690H	60.75	150	1.38	433	3.68	<i>d</i>
Tetrabenzoanthanthrene (VI)	6	3340T 3285 corr.	57.32	3650T 3584 corr.	59.87	285	2.55	-106	-0.88	<i>e</i>
Hexabenzocoronene (III)	7	3600T 3537 corr.	59.48	3875T 3807 corr.	61.65	252	2.16	223	1.78	<i>e</i>

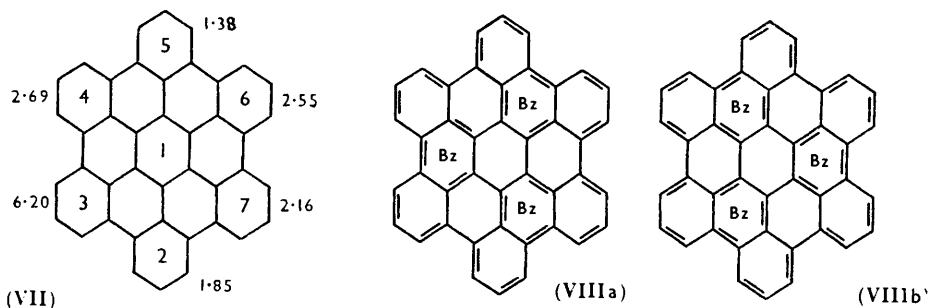
Solvent: V = vapour, A = alcohol, H = heptane, T = trichlorobenzene.

Corr.: corrected for heptane solution: vapour state \rightarrow heptane = -900 cm.^{-1} ; trichlorobenzene \rightarrow heptane = $+500 \text{ cm.}^{-1}$; alcohol \rightarrow heptane = 0 cm.^{-1} .

References: *a*, Scheibe, Povenz, and Lindstrom, *Z. phys. Chem., B*, 1933, 20, 283. *b*, Clar, *Spectrochim. Acta*, 1950, 4, 116. *c*, Clar, *Ber.*, 1943, 76, 613. *d*, Clar and Zander, *J.*, 1958, 1861. *e* this paper.

less suitable because in diphenyl the p -band is superimposed on the α -band. The p -bands involve the localisation of π -electrons in the excited state. Since this localisation takes place in different positions in different hydrocarbons, their comparison does not show any regularities (see Table 1).

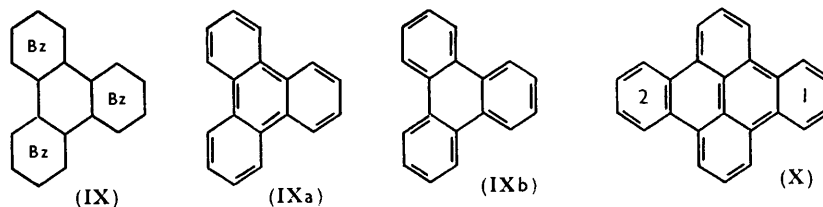
The differences, in \AA or better \AA^\ddagger , the latter being a scale for reciprocal nuclear charges,⁹ show the changing degree of electronic interaction between the benzenoid rings. The β -band of benzene shifts by 1.85\AA^\ddagger in passing to diphenyl as a result of the quasi-single bond or contact bond between the two rings. The transition to triphenylene brings a much bigger shift of 6.20\AA^\ddagger . This could be related to the more highly conjugated structure (IXa) which, unlike (IXb), provides better electronic interaction between the three



external rings through double bonds. The Kekulé structure (IXb) is also one of the eight possible structures contained in formula (IX). The three bonds linking the three external rings in triphenylene can therefore assume single- and double-bond character which is the characteristic of a true aromatic bond.

⁹ Clar, "Aromatische Kohlenwasserstoffe," Springer-Verlag, 1952, pp. 25, 51; Clar and Willicks, *Chem. Ber.*, 1956, 89, 743; Clar and Kühn, *Annalen*, 1956, 601, 181; Boggiano and Clar, *J.*, 1957, 268.

The fourth benzenoid ring in 1 : 2-6 : 7-dibenzopyrene (X) can be connected to structure (IXa) only by two single or contact bonds. Therefore only ring 1 or ring 2 can be linked



to the diphenyl system by two double bonds in formula (X). This would produce a much smaller shift than in passing from diphenyl to triphenylene. It amounts to $2.69 \text{ \AA}^\ddagger$ which is less than double the shift for the contact bond in diphenyl. Thus the two phenylene rings 1 and 2 in dibenzopyrene (X) show a strong asymmetric anellation starting from diphenyl which is quite different from the acene and phene series where the anellation per ring is constant ⁶ in units A^\ddagger . This is also the reason why dibenzopyrene (X) has not the properties of a dibenzotetracene.

Ring 5 in formula (VII) is connected to dibenzopyrene by two contact bonds; the shift associated with them decreases to $1.38 \text{ \AA}^\ddagger$. A similar decrease of the shift is observed in passing from diphenyl to terphenyl in comparison with the shift from benzene to diphenyl. Building up tetrabenzanthanthrene from tribenzoperylene [addition of ring 6 in formula (VII)] involves the formation of another two contact bonds which produce a shift of $2.55 \text{ \AA}^\ddagger$, about the same as that for the formation of the bond between rings 3 and 4 in formula (VII).

The most striking feature of this comparison is the lack of any particular effect when the gap is filled with the formation of the hexagonally symmetrical hexabenzocoronene [*i.e.*, formation of bond between rings 6 and 7 in formula (VII)]. Although the seventh ring is connected through three contact bonds the shift is only $2.16 \text{ \AA}^\ddagger$, corresponding to less than two contact bonds. There is no evidence for the tempting assumption of a rotation of π -electrons through the external frame of 15 alternating double bonds in Kekulé structures (VIIIa) and (VIIIb). Here the six central double bonds would be accommodated in a triphenylene system marked Bz. The 15 external double bonds in (VIIIa) and (VIIIb) alone should shift the β -band as far to the red as in heptaphene ⁷ which is obviously not the case.

Contrary to this, structure (VII) contains the frame of a cyclic *m*-sexiphenyl. It has been shown that the spectrally recorded conjugation in the *m*-polyphenyl series does not extend beyond diphenyl ⁸ which agrees well with the above shifts. The greater part of electronic interchange should therefore result from the six crossed *p*-terphenyl systems and go through the middle ring. This comparison does not support the current assumption that all Kekulé structures contribute equally to the ground state. Many of the possible Kekulé structures [like (VIIIa) and (VIIIb) with four benzenoid rings less than the maximum seven] with a higher degree of conjugation between rings have obviously no influence [except (IXa)] whilst the arrangement of double bonds in benzenoid rings is preferred. The assumption of contact bonds between them accounts satisfactorily for the observed shifts. The comparison also shows the clear difference between a contact bond which cannot become a double bond in terms of Kekulé structures (type found in the central bonds of diphenyl and perylene) and an aromatic bond which can become a single or a double bond (type found in the acenes and phenes).

EXPERIMENTAL

M. p.s were measured in evacuated capillaries. Microanalyses were by J. M. Cameron and his staff.

⁷ Clar and Kelly, *J. Amer. Chem. Soc.*, 1954, **76**, 3502.

⁸ Gillam and Hey, *J.*, 1939, 1170.

2 : 3-7 : 8-*Dibenzoperinaphthene Perbromide*.—Bromine (7.5 g.) in benzene (20 ml.) was added to the dibenzoperinaphthene (I) (5.0 g.) in benzene (100 ml.). The dark brown *perbromide* was filtered off, washed with benzene, and dried in a vacuum at 50° (yield 7.9 g.) (Found: C, 50.8; H, 2.8; Br, 46.8. $C_{21}H_{14}Br_3$ requires C, 49.8; H, 2.8; Br, 47.4%). It decomposed gradually with evolution of hydrobromic acid. When a solution of the perbromide in acetone was cooled dibenzoperinaphthene, m. p. 170°, crystallised in needles. In boiling acetic acid the perbromide formed a mixture of dibenzoperinaphthone, m. p. 208°, and dibenzoperinaphthene which could be separated by crystallisation from xylene and acetic acid. The perbromide melted at 153° with evolution of hydrobromic acid and resolidified immediately; the solid then contained tetrabenzoperopyrene (II). The perbromide gave up bromine when a suspension in nitrobenzene or carbon disulphide was titrated with aqueous sodium thiosulphate (potassium iodide–starch indicator) (Found: 1.6 atoms of Br/molecule in nitrobenzene; 1.8 in carbon disulphide).

4 : 5-6 : 7-11 : 12-13 : 14-*Tetrabenzoperopyrene* (II).—Dibenzoperinaphthene perbromide (3.15 g.) was melted in a vacuum at 153° (Found: loss, 1.38 g. Calc. for 3HBr: 1.51 g.). The powdered melt was sublimed at 400°/0.1 mm.; *tetrabenzoperopyrene* sublimed in orange prisms which were crystallised from trichlorobenzene and xylene (Found: C, 96.0; H, 4.1. $C_{42}H_{22}$ requires C, 95.8; H, 4.2%). It did not dissolve in cold concentrated sulphuric acid, melted at 481–482° with evolution of hydrogen (86% of the calculated volume was collected), and resolidified with formation of hexabenzocoronene (III).

1 : 12-2 : 3-4 : 5-6 : 7-8 : 9-10 : 11-*Hexabenzocoronene* (III).—(a) The crude molten tetrabenzoperopyrene was sublimed at 500°/0.1 mm. *Hexabenzocoronene* sublimed in pale brownish-yellow needles which were recrystallised from boiling pyrene. Hot 1-methylnaphthalene was added to the cooling solution to keep it liquid. Hexabenzocoronene was obtained in long flat needles which were resublimed (Found: C, 96.4; H, 3.5. $C_{42}H_{18}$ requires C, 96.5; H, 3.5%). It did not melt <700° and did not dissolve in concentrated sulphuric acid. It was very slightly soluble in trichlorobenzene. When this solution was cooled in liquid nitrogen and irradiated (mercury lamp) a very strong orange phosphorescence of long life appeared. The short-life blue phosphorescence of trichlorobenzene was easily masked by it.

(b) Dibenzoperinaphthene (I) (2.6 g.) and sulphur (0.64 g.; 2 atomic proportions) were powdered together. When the mixture was melted (at 220°) it evolved hydrogen sulphide and became solid. Xylene was added and the residue filtered off, washed, sublimed from copper at 500°/0.1 mm., and then recrystallised from boiling pyrene. The hydrocarbon was identical with the hexabenzocoronene described above. The yield was variable.

(c) A considerable amount of hexabenzocoronene was obtained when the distillation residue from the preparation of dibenzoperinaphthene ² was powdered, sublimed, and crystallised as described above.

1'-*Phenyl*-1 : 12-2 : 3-10 : 11-*tribenzoperylene* (V).—2 : 3-10 : 11-Dibenzoperylene ¹ (3 g.) and phenylacetylene (5 g.) were refluxed for 3 hr. More phenylacetylene (5 g.) was added and refluxing continued for 7 hr. The suspended dibenzoperylene gradually dissolved and yellow needles, changing to prisms, appeared. The viscous mixture was diluted with xylene (20 ml.), and the crystals (1.3 g.) filtered off. More (0.2 g.) were obtained by evaporation of the xylene and replacing it by ether. The *phenyltribenzoperylene* was crystallised from nitrobenzene–trichlorobenzene and twice from xylene. It formed pale yellow prisms, m. p. 354–356°, and did not dissolve in concentrated sulphuric acid (Found: C, 95.6; H, 4.4. $C_{36}H_{20}$ requires C, 95.5; H, 4.5%). It showed a strong orange-yellow phosphorescence in solid solution in dioxan cooled in liquid nitrogen.

1 : 2-3 : 4-5 : 6-10 : 11-*Tetrabenzanthanthrene* (VI).—Powdered phenyltribenzoperylene (0.3 g.) was added to a melt of sodium chloride (3 g.) and aluminium chloride (15 g.) at 120°. The temperature was raised to 140° and kept for 8 min. Decomposition of the melt with dilute hydrochloric acid gave a yellow precipitate which was filtered off and washed with hot water and ammonia. It sublimed almost completely at 400°/0.1 mm. The sublimate was crystallised twice from trichlorobenzene giving long flat greenish yellow needles, m. p. 434–436°, which did not dissolve in concentrated sulphuric acid (Found: C, 96.1; H, 4.3. $C_{36}H_{18}$ requires C, 96.0; H, 4.0%). They showed a strong yellow phosphorescence of long life in solid solution in dioxan cooled in liquid nitrogen.

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