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Structure and Characterization of 9,10-Diethyl-9,10-diphospha-9,10-dihydroanthracene as an Electron Donor

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The molecular structure of 9,10-diethyl-9,10-diphospha-9,10-dihydroanthracene (PEPP) was determined by X-ray analysis. The central six-membered ring takes a boat conformation with two phosphorus atoms being the stem and stern, and the condensed tricyclic skeleton forms a butterfly-like structure. Of the two ethyl groups, which are attached to two P atoms in the central ring, the one is placed toward outside the skeleton (extra), and the other is located toward the inside of the 'butterfly' (intra). The observed redox potential of 0.63 V vs. Ag/AgCl suggests that this molecule has a fairly good electron-donating characteristics. From the spectroscopic observation and a quantum-chemical calculation, the donating orbital is estimated to be that of lone pair electrons at the P atom that attaches to the intra ethyl group.

'Charge-transfer' is so important a concept that it is concerned with almost all the branches of chemistry. Conventional donor molecules usually possess a π-system (a π donor), or heteroatom with unshared electrons (an n donor), such as O, N, and chalcogen atoms, or a heterocyclic system with both π and n characteristics. In the course of looking for a new donor material, we have been interested in heterocyclic systems including P atoms, which belong to the same group as N. This paper concerns 9,10-diethyl-9,10-diphospha-9,10-dihydroanthracene (PEPP, Chart 1), which is made by substituting at the 9 and 10 positions of anthracene skeleton with two ethylphosphines. We expected to analyze its action as an electron donor as well as its molecular structure.

Experimental

Preparation of PEPP. All the preparation procedures were done under a nitrogen atmosphere. Synthesis of PEPP was done as described in the literature,[1] except for the final stage as stated next. The Grignard reagent was obtained by treating di(*o*-chlorophenyl)ethylphosphine with magnesium in tetrahydrofuran (THF). Then, it was treated with dichloroethylphosphine[2] to give PEPP. It was purified by recrystallization from methanol twice (mp 52.4—53.4 °C). About the minor product (mp 96—97 °C), mentioned by Davis and Mann,[1] we could not obtain even its traces. Colorless and transparent single crystals were grown from methanol by using seed crystals.

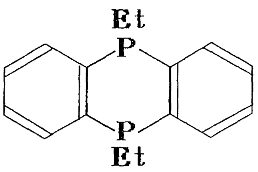

Chart 1.

Acceptor materials, 7, 7, 8, 8-tetracyano-*p*-quinodimethane (TCNQ) and I_2 (Tokyo Kasei Co., Ltd.), were purified by recrystallization from acetonitrile and sublimation, respectively.

X-Ray Data Collection. A columnar crystal about $0.5\times0.5\times0.5$ mm^3 was coated with epoxy adhesive, and mounted on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.71073$ Å). Lattice parameters were determined with 20 ($28°\leqq2\theta\leqq32°$) reflections. Diffraction data were collected in $\theta/2\theta$ mode with scan width $(1+0.35\tan\theta)°$ in θ, scan rate at 4° min^{-1} in θ, and scan range $2\theta_{\max}\leqq60°$. Three standard reflections, (5 6 −4, −10 −1 1, −10 1 1) were monitored at every 100 measurements, and their intensity variations were within 2% in F. Of the 4773 reflections measured, 3243 reflections were observed with $|F_o|>3\sigma(|F_o|)$, and used for refinements.

Structure was solved by the direct method, and refined by block-diagonal least-squares refinement. The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$, with $w=1/\sigma^2(|F_o|)$. Refined parameters are atomic coordinates for all the atoms and anisotropic temperature factors for non-hydrogen atoms. The isotropic temperature factor for hydrogen atoms was fixed at $B_{\text{iso}}=4.0$ Å^2. Residuals were converged to $R=0.052$ and $R_w=0.030$. Scattering factors and the anomalous dispersion factor for P was taken from International Tables for X-ray Crystallography.[3] Calculations were done on a Panafacom U-1200II computer with the Rigaku RASA-5P program package and on a HITAC M-880 at the Computer Centre of the University of Tokyo with the UNICS program system.[4]

Cyclic Voltammetry (CV). Measurements of CV were done with an ADVANTEST TR6142 function generator and a Nikko Keisoku NPOT-2501 potentiostat. The working and counter electrodes were a platinum circular disk (10 mmϕ) and a platinum wire (1 mmϕ), respectively. As a supporting electrolyte, tetrabutylammonium perchlorate (0.1 mol dm^{-3}) was used in acetonitrile. An aqueous Ag/AgCl electrode (Toa Elec. Co., Ltd. HS-305DS) was used as a reference electrode with a salt bridge of a saturated aqueous solution of KCl. Solvents were degassed by repeated freezing and pumping under a nitrogen atmosphere.

Electronic Absorption Spectra. Measurements were done with a Hitachi 330 spectrometer with the degassed acetonitrile for the solvent.

Quantum-Chemical Calculation. Molecular orbital calculation and structure optimization by the PM3 method were done with MOPAC Ver. 6.01[5] on a HITAC M-880 at the Computer Centre of the University of Tokyo. All the calculations were done by using the keywords "PRECISE" and "NODIIS". Calculations of PEPP$^+$ were done with the unrestricted Hartree–Fock equation and others were done with a restricted Hartree–Fock equation.

Complex Formation Both acetonitrile solutions (1×10^{-3} mol dm^{-3}) of PEPP and acceptor (TCNQ or I_2), were mixed at about 1 : 2 mol ratio. By slow evaporation of the solvent in a dry atmosphere, black powder complexes were obtained.

Electrical Resistivity. Electrical resistivity was measured by a two-probe method with compaction pellets. Carbon paint was applied as the contacts between electrodes (25 μmϕ gold wire) and specimens.

Results and Discussion

Molecular Structure. Crystal data: $C_{16}H_{18}P_2$, F. W. =272.27, monoclinic, space group $P2_1/c$, $a=13.865(2)$, $b=11.258(2)$, $c=9.537(2)$ Å, $\beta=95.89(2)°$, $V=1480.7(5)$ Å^3, $Z=4$, $D_x=1.22$ Mg m^{-3}, $\mu(\text{Mo }K\alpha)=0.276$ mm^{-1}. The molecular structure is shown in Fig. 1 with the atom numbering. Table 1 describes atomic parameters and Table 2 gives selected geometrical parameters.[7] The central six-membered ring is in a boat conformation with the two P atoms being stem and stern, and the condensed tricyclic skeleton forms a 'butterfly-like' structure. The dihedral angle between the external two benzene rings is 144.8°. Of the two ethyl groups, each of which is attached to the individual P atom in the central ring, the one (attached to P(1)) is towards outside the skeleton ('extra' position), and the other (attached to P(2)) is placed towards inside the 'butterfly' ('intra' position), though both ethyl groups take axial position to the six-membered ring.[8] Thus, the conformation of this molecule is intra-extra as opposed to the estimation of the intra-intra structure by Davis and Mann.[1] The different vicinity between the two ethyl groups perhaps reflects the significantly different angles between C–P(1)–C's and C–P(2)–C's. In any case, the bonding directions of a P atom are tetrahedral including its lone pair electrons. All the other bond lengths and angles are in the normal range. The slightly shorter lengths of P–C(ring)'s than those of P–C(ethyl)'s probably depend on the effects of neighboring benzene rings.

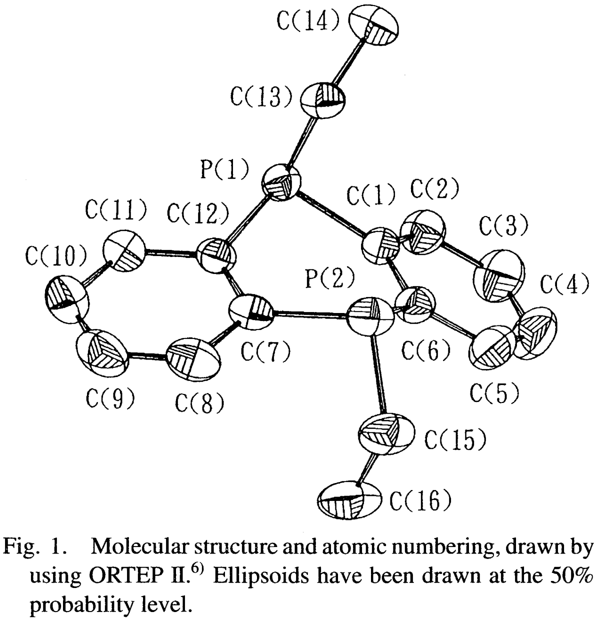

Fig. 1. Molecular structure and atomic numbering, drawn by using ORTEP II.[6] Ellipsoids have been drawn at the 50% probability level.

Table 1. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for Non-Hydrogen Atoms, with Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}[a]/Å^2
P(1)	0.72370(3)	0.08745(4)	0.24527(5)	2.82(1)
P(2)	0.74486(4)	−0.09629(5)	0.53067(5)	3.54(1)
C(1)	0.8321(1)	−0.0007(1)	0.3002(2)	2.84(5)
C(2)	0.9112(1)	0.0164(2)	0.2216(2)	3.76(6)
C(3)	0.9973(1)	−0.0446(2)	0.2547(2)	4.99(7)
C(4)	1.0051(1)	−0.1236(2)	0.3649(2)	5.27(7)
C(5)	0.9280(1)	−0.1419(2)	0.4430(2)	4.41(6)
C(6)	0.8402(1)	−0.0810(2)	0.4123(2)	3.08(5)
C(7)	0.6347(1)	−0.0866(2)	0.4088(2)	3.15(5)
C(8)	0.5516(1)	−0.1504(2)	0.4377(2)	4.42(6)
C(9)	0.4650(1)	−0.1391(2)	0.3518(2)	5.07(7)
C(10)	0.4581(1)	−0.0647(2)	0.2371(2)	4.92(7)
C(11)	0.5389(1)	−0.0005(2)	0.2076(2)	3.96(6)
C(12)	0.6269(1)	−0.0096(1)	0.2933(2)	2.92(5)
C(13)	0.7282(1)	0.1976(1)	0.3895(2)	3.09(5)
C(14)	0.8001(1)	0.2965(2)	0.3653(2)	4.15(6)
C(15)	0.7500(1)	−0.2567(2)	0.5753(2)	4.69(6)
C(16)	0.7430(2)	−0.3444(2)	0.4539(2)	5.69(7)

a) $B_{\text{eq}}=(4/3)\sum_i\sum_j B_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

Oxidation Potential. The first oxidation potential (represented by the first anodic peak potential: $E_\text{p}{}^{\text{o1}}$) of PEPP was observed as 0.63 V vs. Ag/AgCl. This value suggests that the molecule possesses a donating character to a similar extent to that of benzo[a]phenothiazine and/or benzo[c]phenothiazine, since both of their $E_\text{p}{}^{\text{o1}}$'s have been observed as 0.62 V vs. Ag/AgCl under almost the same conditions as this material.[9] With regard to PEPP, however, the second anodic peak $E_\text{p}{}^{\text{o2}}$ (at about 1.12 V vs. Ag/AgCl) was not always clearly recognizable and the cathodic peaks ($E_\text{p}{}^{\text{r1}}$ and $E_\text{p}{}^{\text{r2}}$) were very ambiguous, though the $E_\text{p}{}^{\text{o1}}$ value was reproducible. These facts mean that redox of PEPP is not a complete reversible process under these experimental conditions.

$E_\text{p}{}^{\text{o1}}$ and $E_\text{p}{}^{\text{o2}}$ of ethyldiphenylphosphine ($EtPPh_2$), which lacks a central six-membered ring and was used for a comparison of PEPP, were obtained as 0.85 and 1.30 V vs. Ag/AgCl with good reproducibility, except for ambiguous $E_\text{p}{}^{\text{r1}}$. Thus, the comparatively low value of $E_\text{p}{}^{\text{o1}}$, the unstable second oxidation state and incomplete redox process of PEPP are probably due to the presence of its second P atom in PEPP.

Electronic Spectra. Figure 2 shows typical elec-

Table 2. Bond Distances (Å) and Angles (°) of PEPP

P(1)–C(1)	1.832(2)	P(1)–C(12)	1.825(2)
P(1)–C(13)	1.848(2)	P(2)–C(6)	1.832(2)
P(2)–C(7)	1.825(2)	P(2)–C(15)	1.855(2)
C(1)–C(2)	1.404(3)	C(1)–C(6)	1.396(2)
C(2)–C(3)	1.385(3)	C(3)–C(4)	1.373(3)
C(4)–C(5)	1.380(3)	C(5)–C(6)	1.402(3)
C(7)–C(8)	1.409(3)	C(7)–C(12)	1.397(2)
C(8)–C(9)	1.388(3)	C(9)–C(10)	1.373(3)
C(10)–C(11)	1.385(3)	C(11)–C(12)	1.402(3)
C(13)–C(14)	1.528(3)	C(15)–C(16)	1.517(3)
C(1)–P(1)–C(12)	101.93(8)	C(1)–P(1)–C(13)	100.75(8)
C(12)–P(1)–C(13)	100.63(8)	C(6)–P(2)–C(7)	102.21(8)
C(6)–P(2)–C(15)	102.69(9)	C(7)–P(2)–C(15)	102.37(9)
P(1)–C(1)–C(2)	115.9(1)	P(1)–C(1)–C(6)	124.7(1)
C(2)–C(1)–C(6)	119.5(2)	C(1)–C(2)–C(3)	120.8(2)
C(2)–C(3)–C(4)	119.6(2)	C(3)–C(4)–C(5)	120.4(2)
C(4)–C(5)–C(6)	121.2(2)	P(2)–C(6)–C(1)	121.8(1)
P(2)–C(6)–C(5)	119.4(1)	C(1)–C(6)–C(5)	118.5(2)
P(2)–C(7)–C(8)	119.5(1)	P(2)–C(7)–C(12)	122.1(1)
C(8)–C(7)–C(12)	118.2(2)	C(7)–C(8)–C(9)	120.9(2)
C(8)–C(9)–C(10)	120.8(2)	C(9)–C(10)–C(11)	119.2(2)
C(10)–C(11)–C(12)	121.1(2)	P(1)–C(12)–C(7)	124.7(1)
P(1)–C(12)–C(11)	115.4(1)	C(7)–C(12)–C(11)	119.8(2)
P(1)–C(13)–C(14)	110.4(1)	P(2)–C(15)–C(16)	117.4(2)

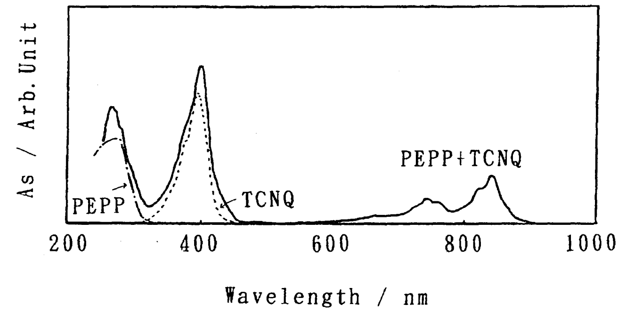

Fig. 2. Absorption spectra of neutral PEPP (–•–), neutral TCNQ (- - -), and their mixed solution (—) in methanol.

tronic absorption spectra of the neutral solutions of PEPP and TCNQ, along with those of a mixed solution of them. Though the neutral solutions of PEPP and TCNQ are colorless and yellow-colored, respectively, the mixed solution turned green in a few minutes. Since the new peaks at 744 and 842 nm can be assigned as those of $TCNQ^-$,[10] $PEPP^+$ or $PEPP^{n+}$ ($n \geqq 2$) should exist in the mixed solution. However, neither significant deformation in the peak of PEPP at 265 nm nor new bands at longer wavelengths are observed in the mixed solution. So, the spectral results suggest that PEPP molecule does not extend its π-conjugation system over the whole molecule in its cation state.

Quantum-Chemical Calculation. To estimate the donating orbitals of this molecule, the optimized structures of neutral PEPP, $PEPP^+$, and $PEPP^{2+}$ were calculated by the MOPAC PM3 program. Table 3 includes averaged calculated geometrical parameters around the two P atoms together with the observed data by X-ray analysis. It is noteworthy that the calculated results of neutral PEPP appreciably agree with the observed values except for the dihedral angle. And the optimized configuration of neutral molecule is also an intra-extra structure, being identical with the observed result. By being oxidized to $PEPP^+$ or $PEPP^{2+}$, geometrical changes around P atoms are not so significant for the extra, but fairly large for the intra conformation. Namely, only the P atom in the intra part tends to change its geometry from tetrahedral to planar geometry, that is, from sp^3 to an sp^2 hybrid state by oxidation. In other words, the extra conformation could be more stable than the intra conformation, and only the orbital of lone pair electrons at the intra P atom plays a role of a donating orbital without being spread into the conjugation system throughout the whole molecule. Obviously, the molecular structures of neutral PEPP and phenothiazine (PT) are very similar. It has been known, however, that phenothiazinium ion (cation radical of PT) can stably exist either in solution or in solid states, in contrast to the case of PEPP.[11,12] On the basis of structural considerations, the stability of $PT^{+\bullet}$ has been ascribed to its central thiazine ring being conjugated.[12—15] The difference in the stability between these two cations should be due to the difference in the easiness for the conjugation in the whole molecule. Though PEPP loses its electron to form a cation or cation radical very easily, the produced chemical entity is not necessarily stable. This is the reason why the $E_p{}^{o1}$ value of PEPP is lower than that of $EtPPh_2$ by 0.2 V, as mentioned in the above section.

Complex Formation. Solid charge-transfer complexes were obtained for TCNQ and iodine by using this material. They possess semiconducting properties: their electrical resistivity in a compact pellet was estimated as 10^3 and 10^6 Ω cm for I_2 and TCNQ complexes, respectively.

Table 3. Calculated Bond Distances (Å) and Angles (°) around the P Atoms

Molecule	P–C(Ph)[a]		P–C(Et)		C(Et)–P–C(Ph)[a]		C(Ph)–P–C(Ph)		Dihedral angle[b]
	extra	intra	extra	intra	extra	intra	extra	intra	
PEPP^0									
calcd	1.855	1.853	1.897	1.904	101.6	103.0	103.8	103.9	159.7
obsd[c]	1.829	1.829	1.848	1.855	100.7	102.5	101.9	102.2	144.8
PEPP$^+$	1.865	1.702	1.883	1.810	102.5	115.7	102.8	115.2	176.7
PEPP^{2+}	1.874	1.600	1.869	1.719	104.3	119.6	100.2	120.8	173.0

a) Average value of the two equivalent bondings. b) Calculated between the two external benzene rings. c) Obtained from X-ray data.

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