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7-Diazo-7*H*-benz[*de*]anthracene and 7*H*-Benz[*de*]anthracen-7-ylidene

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7-Diazo-7*H*-benz[*de*]anthracene has been prepared by the HgO oxidation of the corresponding hydrazone in ether. The yellow-green diazo compound in a 2-methyltetrahydrofuran matrix has been photolyzed with a high-pressure mercury lamp in an ESR cavity at 14 K. From the X, Y, and Z transitions due to the unoriented triplet species, the zero-field splitting parameters of 7*H*-benz[*de*]anthracen-7-ylidene have been determined: $|D|=0.2662$ and $|E|=0.0175\,\mathrm{cm}^{-1}$. A temperature dependence experiment showed linear signal intensities *vs.* $1/T$ plots, indicating that the carbene is in the ground triplet state. The zero-field splitting parameters have been theoretically calculated by assuming the dipolar interaction of the electron spins one on the n-orbital at the 7-position and the other delocalized on the Hückel π-framework.

High-spin organic molecules are of recent interest as a model for organic ferromagnets.[1] Special attention has been devoted to antiaromatic annulenes[2] and polyradicals.[3] Our approach to the subject is characterized by the construction of polycarbenes by taking advantage of triplet diphenylcarbene as an appropriate building block.[4] Thus the nonet ground state of a tetracarbene, *m*-phenylenebis((diphenylmethylen-3-yl)methylene), has been generated and characterized by ESR spectroscopy.[5] In order to develop magnetic organic materials of interest, there remain several difficulties to overcome. The increase of the spin multiplicity and the thermal stability of the polycarbenes is one of the few important factors. As a part of these efforts, we have scrutinized several new carbenes to be used as a unit. In this paper, we report the preparation of the diazo compound and generation of the triplet carbene derived from 7*H*-benz[*de*]anthracen-7-one. The ESR spectra of the carbene have also been fully analyzed.

Results and Discussion

*Preparation of 7-Diazo-7*H*-benz[*de*]anthracene.* The diazo compound was prepared by typical mercury(II) oxide oxidation of the corresponding hydrazone which in turn was obtained by sluggish reaction of 7*H*-benz[*de*]anthracen-7-one with hydrazine hydrate. The yellow-green diazo compound crystallized in fine prisms. A characteristic IR band was observed at $2030\,\mathrm{cm}^{-1}$. UV absorptions due to the π-π^* and n-π^* transitions were observed at 407 ($\log \varepsilon=4.14$), 425 (4.10) and 600 nm (2.42), respectively. The 400 MHz ^{1}H NMR spectrum exhibited first-order multiplets (Fig. 1) which were analyzed by the standard decoupling technique. The upfield shifts of the hydrogens peri to the diazo group are noted. The corresponding hydrogens of the precursor ketone appear in the lowest field.

*Photochemical Generation and ESR Characterization of 7*H*-Benz[*de*]anthracen-7-ylidene.* 7-Diazo-7*H*-benz[*de*]anthracene in 2-methyltetrahydrofuran matrices was irradiated with a high-pressure mercury lamp in an ESR cavity at 14 K. The resulting ESR spectrum obtained at 9.332 GHz is reproduced in Fig. 2. The signals are typical fine structure patterns for unoriented triplet species. Signals at 420.9, 485.5, and 617.5 mT are assigned to a set of the high-field X, Y, and Z transitions from which the zero-field splitting parameters were obtained as $|D|=0.2662$ and $|E|=0.0175\,\mathrm{cm}^{-1}$ by solving Eqs:[6a]

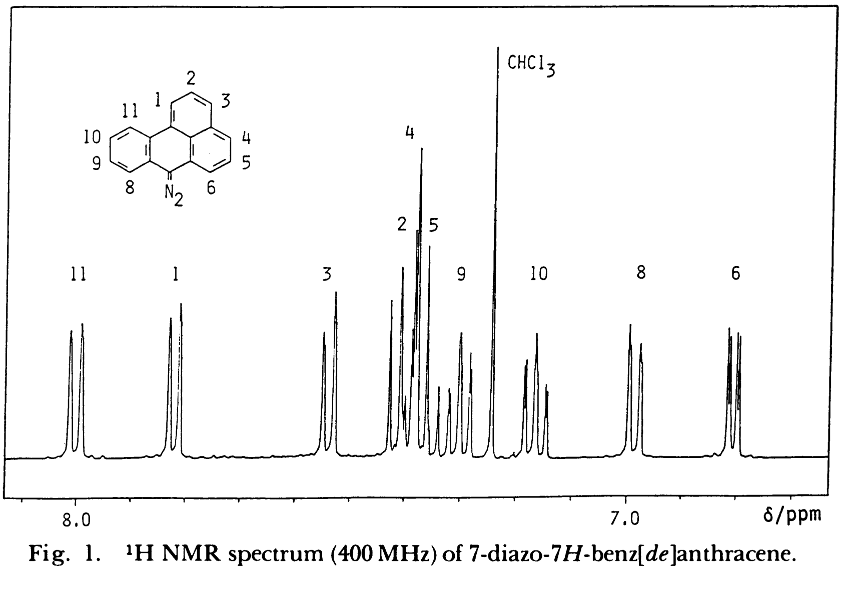


Fig. 1. ^{1}H NMR spectrum (400 MHz) of 7-diazo-7*H*-benz[*de*]anthracene.

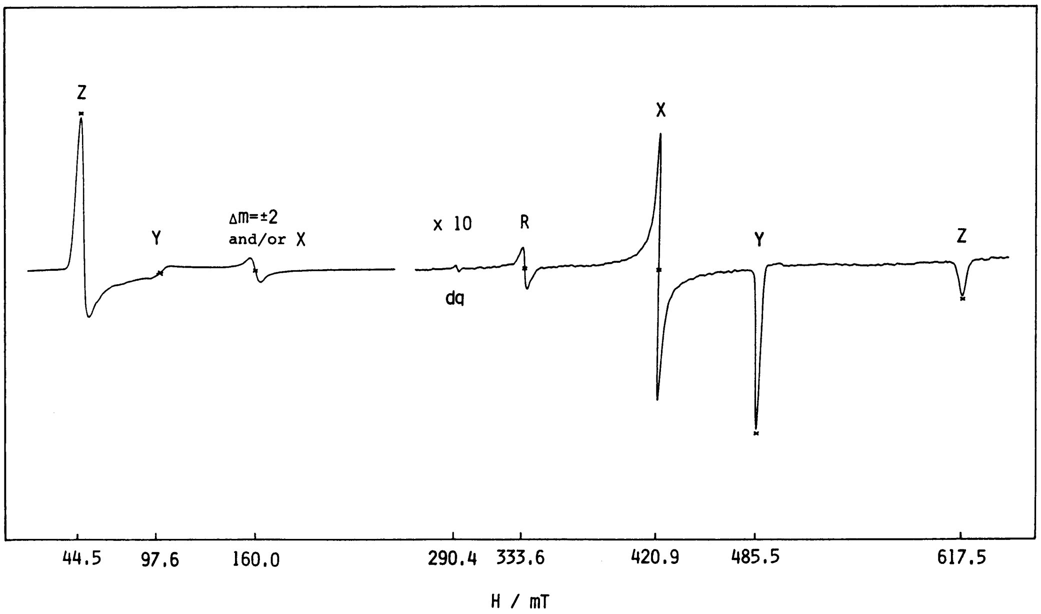


Fig. 2. ESR spectrum (9.332 GHz) obtained by photolysis of 7-diazo-7*H*-benz[*de*]-anthracene in 2-methyltetrahydrofuran glass at 14 K.

$$(g\beta H_X)^2 = (g_e/g_{XX})^2[(g\beta H_0 \pm D \mp E)(g\beta H_0 \mp 2E)]$$
$$(g\beta H_Y)^2 = (g_e/g_{YY})^2[(g\beta H_0 \pm D \pm E)(g\beta H_0 \pm 2E)] \quad (1)$$
$$(g\beta H_Z)^2 = (g_e/g_{ZZ})^2[(g\beta H_0 \pm D)^2 \mp E^2].$$

The corresponding low-field X, Y, and Z transitions were calculated from these zero-field parameters using Eqs. 1 to give the resonance fields 157.4, 93.5, and 44.5 mT, respectively. These values agree reasonably well with the observed low-field transitions as shown in Fig. 2. The resonance at 160 mT which was assigned to the X transition may contain the signal due to $\Delta m = \pm 2$ transition. Other signals at 290.4 and 333.6 mT are assigned to the double quantum transition of the carbene and a normal resonance due to fortuitous doublet species, respectively.

The D values of typical diarylcarbenes are in the range 0.41—0.37 cm^{-1}. With the exception of di(9-anthryl)methylene (D=0.113 cm^{-1} at 4 K),6b) the D parameter of 7*H*-benz[*de*]anthracen-7-ylidene obtained in this study is the smallest ever reported, showing extensive delocalization of the odd electron in the π-framework of the molecule.

The temperature dependence of the ESR signal intensity of the low-field Z transition in the range 15—77 K obeyed the Curie-Weiss linear plot (Fig. 3). The triplet carbene is concluded not to be thermally populated from the ground state singlet. In 2-methyltetrahydrofuran matrices, the ESR signals started to disappear at 85 K. In powdered crystals which gave birth to 7*H*-benz[*de*]anthracen-7-ylidene on irradiation ($|D|$=0.2608 and $|E|$=0.0181 cm^{-1}), it was stable up until 205 K. The thermal stability of the carbene due to delocalization of the odd electron in the π-orbital was not so satisfactory as it was expected.

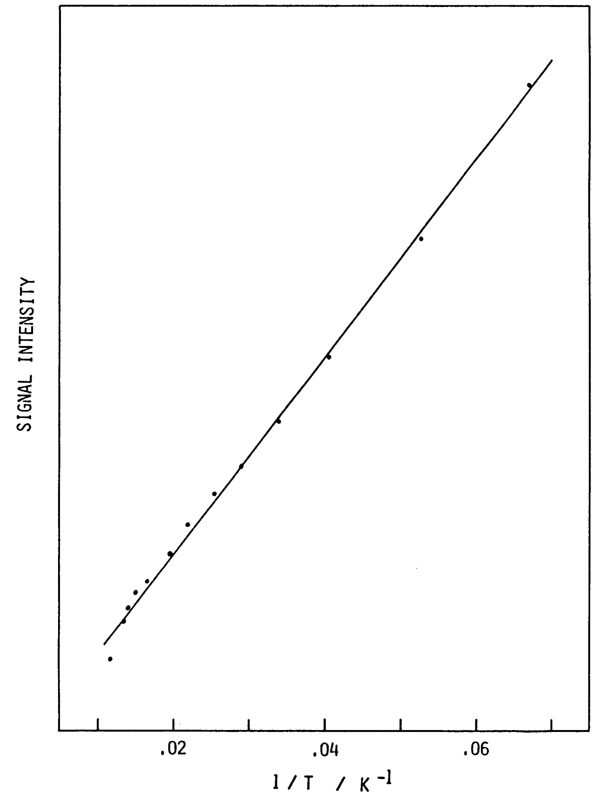


Fig. 3. Plots of signal intensity of the lowfield Z line of 7*H*-benz[*de*]anthracen-7-ylidene *vs.* 1/*T*.

Calculation of the Zero-field Splitting Parameters. The zero-field splitting parameters D and E have been calculated theoretically by the point dipole approximation; only the two-center Coulomb term in the single configuration approximation was considered. The sites of the point electron spins were empirically fixed according to the method of Hutton and Roth7) for the reason of simplicity and empirical reproducibility. Thus the electron spin in the π-orbitals was simulated by two point spins in the π-

lobes located 0.821 Å above and below and molecular plane, each with a half of the spin density on the atom. The σ-electron spin was assumed to be localized on the divalent carbon and expressed by two point spins in the sp^2-orbital placed at ±0.876 Å from the carbon atom with the spin density of 0.7 in the negative lobe and 0.3 in the positive lobe.⁷⁾ The molecular geometry used in the calculation was constructed by the C–C bond distance of 1.40 Å and the bond angles of 120°.

Since the spin-orbit coupling of the two electrons is considered not to contribute to the zero-field parameters in carbenes containing only first-row atoms,⁸⁾ only the dipolar spin-spin interaction was taken into consideration. The spin-spin Hamiltonian is described by Eq. 2:

$$H_{ss} = S\mathbf{D}S, \tag{2}$$

where S is the total spin operator and $\mathbf{D}$ is the dipolar coupling tensor, the elements of which are obtained by the summation of the interactions of each σ spin with each π spin. When the matrix is diagonalized, the zero-field splitting parameters D and E are calculated as Eqs. 3:

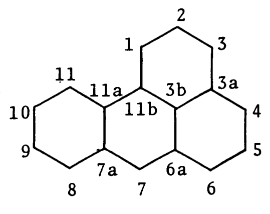
$$\begin{aligned} D &= -\frac{3}{2}Z, \\ E &= -\frac{1}{2}(X-Y), \end{aligned} \tag{3}$$

where $-X$, $-Y$, and $-Z$ are the components of the diagonalized matrix.

As in the calculation by Hutton and Roth,⁷⁾ it was assumed that the π spin density distribution was equal to that in the corresponding radical 7*H*-benz[*de*]anthracen-7-yl. We obtained the spin densities of the radical by the McLachlan method with the use of the zero-order spin densities derived from the Hückel molecular orbital (HMO) theory; the usual HMO parameters α_0 and β_0 were employed in all the carbon atoms and C–C bonds, respectively.

TABLE 1. THE π SPIN DENSITIES OF 7*H*-BENZ[*de*]ANTHRACEN-7-YL USED FOR CALCULATION OF THE π SPIN DISTRIBUTION IN 7*H*-BENZ[*de*]ANTHRACEN-7-YLIDENE

Atom	Spin density	Atom	Spin density
1	0.1456	7	0.3567
2	−0.0512	7a	−0.0478
3	0.1502	8	0.0901
3a	−0.0459	9	−0.0362
3b	0.0149	10	0.0798
4	0.2385	11	−0.0370
5	−0.0745	11a	0.0792
6	0.2441	11b	−0.0433
6a	−0.0632		



The π spin density distribution calculated by the above method is shown in Table 1. The spin density is found to be delocalized mostly in the naphthalene moiety. With the use of the values in Table 1, the dipolar interaction matrix $\mathbf{D}$ was calculated and diagonalized.⁹⁾ The zero-field splitting parameters were obtained according to Eqs. 3: D=0.2486 and E=0.0130 cm^{-1}. The agreement with the experimental values is commendable.

The spin delocalization in the π system and consequent low density at C-7 (0.357) account for the low D value. The spin distribution in the naphthalene ring of 7*H*-benz[*de*]anthracen-7-ylidene carries an interesting implication as regards the magnetic interaction between the molecules in crystal packing. It is usually the case for organic molecules in the crystal field to have the intermolecular distances governed by the van der Waals interaction. At these distances (~4 Å), the exchange interaction between the electron spins on the neighboring molecules tends to be negative. The more stable Coulomb interaction under these conditions is the α spins of one molecule facing the β spins of the other. Therefore, if the molecules of 7*H*-benz[*de*]anthracen-7-ylidene take the superimposable stacking has the crystals, the different spins (α and β) will develop between the two neighboring triplet molecules and the intermolecular interaction should become antiferromagnetic. On the other hand, if the parallel stacking has the phase shift or inversion as shown in Fig. 4, the α *vs.* β relationship holds in the overlapping naphthalene moieties with the high σ and π spin densities at the 7-position having the same sign of spins. The interaction could now become ferromagnetic. Thus the crystal structure of these and other aromatic diazo compounds is of interest and under current study in these laboratories.

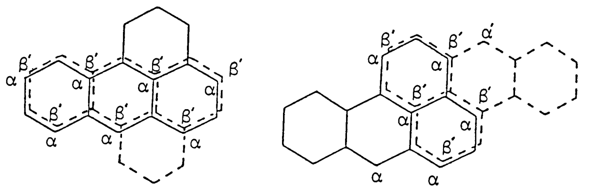


Fig. 4. Some molecular stacking models for potentially ferromagnetic molecular interaction.

Experimental

7H-*Benz[*de*]anthracen-7-one Hydrazone.* A mixture of 7*H*-benz[*de*]anthracen-7-one (2.00 g, 8.70 mmol), zinc chloride (3.60 g, 26.5 mmol) and 30 cm³ of hydrazine hydrate in 60 cm³ of ethylene glycol was refluxed with stirring for 12 h, poured into 200 cm³ of water, and extracted with dichloromethane. The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was chromatographed on alumina and eluted with dichloromethane. Recrystallization from hexane gave 1.16 g (55%) of yellow microcrystalline needles; mp 126—127 °C; IR (KBr) 1630 (C=N), 3180, 3320

(NH_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.41 (t, *J*=7.0 Hz, 1H), 7.44 (t, *J*=7.0 Hz, 1H), 7.62 (dd, *J*=7.3, 8.2 Hz, 1H), 7.63 (dd, *J*=7.3, 8.2 Hz, 1H), 7.82 (d, *J*=8.2 Hz, 1H), 7.88 (d, *J*=8.2 Hz, 1H), 8.08 (d, *J*=7.0 Hz, 1H), 8.17 (d, *J*=7.0 Hz, 1H), 8.22 (d, *J*=7.3 Hz, 1H) and 8.41 (d, *J*=7.3 Hz, 1H).

Found: C, 83.88; H, 4.87; N, 11.41%. Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47%.

7-Diazo-7H-benz[de]anthracene. Yellow mercury(II) oxide (1.8 g, 8.3 mmol), anhydrous sodium sulfate (2.0 g) and five drops of a freshly prepared saturated solution of potassium hydroxide in absolute ethanol were added to a solution of 0.20 g (0.82 mmol) of *7H*-benz[*de*]anthracen-7-one hydrazone in 20 cm^3 of dry tetrahydrofuran at room temperature. The mixture was stirred for 1.5 h in the dark. Inorganic salts were removed by filtration and the solution was concentrated under reduced pressure at room temperature to give 0.2 g (quantitative yield) of yellow-green powder. The product was already spectroscopically pure. The analytical sample was prepared by recrystallization from ether; mp 98—100 °C (decomp); IR (KBr) 2030 cm^{-1}; UV (ether) 269 (log ε 4.53), 285 (4.37), 327 (3.93), 407 (4.14), 425 (4.10), and 600 nm (2.42); ^{1}H NMR ($CDCl_3$) δ=6.81 (d, *J*=6.7 Hz, 1H), 6.97 (d, *J*=7.9 Hz, 1H), 7.16 (dd, *J*=7.6, 8.3 Hz, 1H), 7.30 (dd, *J*=7.9, 8.3 Hz, 1H), 7.36 (dd, *J*=6.7, 8.8 Hz, 1H), 7.39 (d, *J*=8.8 Hz, 1H), 7.41 (dd, *J*=7.3, 8.2 Hz, 1H), 7.54 (d, *J*=8.2 Hz, 1H), 7.82 (d, *J*=7.3 Hz, 1H), and 8.00 (d, *J*=7.6 Hz, 1H).

Found: C, 84.22; H, 4.45; N, 11.58%. Calcd for $C_{17}H_{10}N_2$: C, 84.27; H, 4.16; N, 11.57%.

Spectral Measurements. IR spectra were recorded on a JASCO IR-810 spectrometer. NMR spectra were obtained on a JNM GX-400 spectrometer (400 MHz for ^{1}H) using tetramethylsilane as an internal standard. UV spectra were measured on a HITACHI 340 spectrometer.

ESR spectra were measured on a Varian E-112 spectrometer (X-band microwave unit, 100 kHz field modulation) equipped with an Air Products LTD-3-110 liquid helium transfer system. The diazo compound (*ca.* 2 mg) was dissolved in 2-methyltetrahydrofuran (0.5 cm^3) and the solution was degassed in a quartz cell by three freeze-thaw cycles. The sample was rapidly cooled in a pre-cooled ESR cavity and irradiated with a high-pressure mercury lamp (500 W) at 14 K. The signals due to the triplet carbene appeared immediately after the start of irradiation. The resonance magnetic field values of the signals were measured with the aid of a Varian E500 NMR gauss meter. The dependence of the signal intensities on temperatures was measured by the use of a temperature controlling accessory. The low-field Z line (at 44.5 mT at 14 K) was scanned repeatedly at several temperatures and the peak heights were plotted against $1/T$. In a separate run, the diazo compound (5 mg) was mixed with *7H*-benz[*de*]anthracen-7-one (100 mg) in a mortar with a pestle made of agate, and the mixture was placed in a quartz sample tube (5 mm o.d.) 2 cm in height from the bottom. The sample was irradiated in an ESR cavity to obtain the spectrum of the triplet species.

Theoretical Calculations. Calculations were carried out on a Hitachi M-200H computer, using the program named "Huckel Molecular Orbirtal Calculation" programmed by Dr. H. Kihara and filed in the Program Library of the Computer Center of the Institute for Molecular Science. The McLachlan correction parameter λ was set at 1.2 in the program.

We wish to thank Dr. T. Sugawara of these laboratories for his helpful comments during this work. A collaboration of Prof. R. D. McKelvey in the preliminary preparation of the hydrazone is acknowledged.

References

1) In the chemistry briefing made to the White House Office of Science and Technology Policy, the G. C. Pimentel Committee to Survey Opportunities in the Chemical Sciences put chemical reactivity as one of the priority areas. As an example of the fundamental questions to be answered in the chemical reactivity studies, the possibility of organic ferromagnetic compounds is mentioned (Chemical and Engineering News, January 2, 1984, pp. 8—39).

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6) a) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964); b) E. Wasserman, V. J. Kuck, W. A. Yager, R. S. Hutton, F. D. Greene, V. P. Abegg, and W. M. Weinshenker, *J. Am. Chem. Soc.*, **93**, 6335 (1971).

7) R. S. Hutton and H. D. Roth, *J. Am. Chem. Soc.*, **104**, 7395 (1982). These approximations were first employed to assign the spin density distributions obtained for fluorenylidene by the ENDOR method.[8] Later the empirical values were modified by Hutton and Roth to reproduce the zero-field splitting parameters of methylene. The latter values were used in this study. Since the triplet carbene discussed here is considered to have a smaller bond angle at the divalent carbon owing to the constraint of the ring, a new set of parameters should have been introduced to obtain better agreement with the experimental *D* and *E* values.

8) See for example: C. A. Hutchison, Jr. and G. A. Pearson, *J. Chem. Phys.*, **47**, 520 (1967).

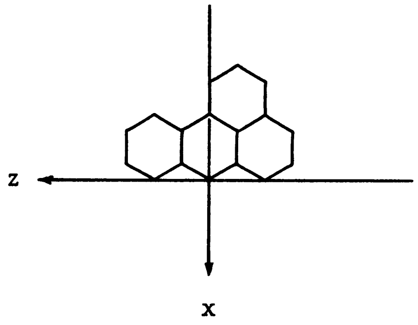
9) In the concrete, the dipolar interaction matrix in Eq. 2 for *7H*-benz[*de*]anthracen-7-ylidene was given by Eq.:

$$\boldsymbol{D} = \frac{(g\beta)^2}{2}\begin{bmatrix} \dfrac{r^2-3x^2}{r^5} & \dfrac{-3xy}{r^5} & \dfrac{-3xz}{r^5} \\ \dfrac{-3xy}{r^5} & \dfrac{r^2-3y^2}{r^5} & \dfrac{-3yz}{r^5} \\ \dfrac{-3xz}{r^5} & \dfrac{-3yz}{r^5} & \dfrac{r^2-3z^2}{r^5} \end{bmatrix}$$

$$= \begin{bmatrix} -0.0699 & 0.0 & -0.0029 \\ 0.0 & -0.0958 & 0.0 \\ -0.0029 & 0.0 & 0.1657 \end{bmatrix}$$

The calculation was made on the assumption that the molecular plane makes the *xz* plane and the origin of the coordinates is at the atom 7 (*i.e.* divalent carbon). The off-

diagonal elements in the above matrix are so small that, after diagonalization, the values of the diagonal elements are little changed.



The coordinate systm given here was arbitrarily taken for convenience of calculations and different from the principal axes *X*, *Y*, and *Z* of the carbene molecule. Conventionally used **H** was employed in a unit of mT throughout this paper to represent magnetic fux density **B**.