2762 © 1980 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 53, 2762—2767 (1980) [Vol. 53, No. 10

Thermochemical Estimation of Destabilization Energies of 1,2-, 1,3-, and 1,4-Dicyanobenzenes Due to Interactions between Substituents. Appendix: Dipole Moments in Solution of the Dicyanobenzenes[†]

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(Received March 7, 1980)

Enthalpies of combustion of 1,2-, 1,3-, and 1,4-dicyanobenzenes were determined by precision oxygen-bomb calorimetry. Enthalpies of sublimation of these compounds were obtained by the measurement of temperature dependence of vapor pressure. The standard enthalpies of combustion $\Delta H_c^\circ(298.15\ \mathrm{K})/\mathrm{kJ\ mol^{-1}}$ and the standard enthalpies of sublimation $\Delta H_s^\circ(298.15\ \mathrm{K})/\mathrm{kJ\ mol^{-1}}$ are as follows: -4000.36 ± 0.67 and 86.9 ± 1.5 for 1,2-dicyanobenzene; -3992.29 ± 0.75 and 90.1 ± 1.5 for 1,3-dicyanobenzene; -3988.04 ± 0.59 and 88.8 ± 1.5 for 1,4-dicyanobenzene, respectively. Thermochemical destabilization energies were estimated by comparing the derived standard enthalpies of formation in gaseous state with those estimated for hypothetical non-destabilized molecules. They were discussed in terms of electrostatic interactions between highly electronegative and dipolar cyano substituents on one and the same benzene ring. Dipole moments of the dicyanobenzenes in benzene and dioxane solutions are reported in Appendix.

Determination of standard enthalpy of formation in gaseous state of a compound is the essentially sole experimental method to evaluate intramolecular energy of molecules. The method has been applied for polyhalobenzenoid compounds to study the interaction energies between substituents by Cox *et al.*,[1,2] who have shown the need to take account of electrostatic interactions between the substituents in the interpretation of standard enthalpies of formation in gaseous state.

As is well-known, a cyano group as well as halogen atoms is highly electronegative substituent. In addition, a cyano group is considered to be dipolar by itself. Thus, a cyano group has been situated at the most electronegative end of general electronegativity sequence of substituents.[3] Cyanohydrocarbons exhibit dipole moments higher than 3 Debye[††] as a rule.

This study has been carried out to elucidate the interaction between cyano substituents on one and the same benzene ring. For this purpose, the standard enthalpies of combustion of 1,2-, 1,3-, and 1,4-dicyanobenzenes each in the crystalline state were measured by oxygen bomb calorimetry. Enthalpies of sublimation of the compounds were determined from the measurement of temperature dependence of vapor pressure. In this paper, results of the calorimetric and vapor pressure measurements are reported. From standard enthalpies of formation in gaseous state thus derived, destabilization energies were estimated and discussed in terms of electrostatic interactions between cyano substituents on the same benzene ring.

Experimental

Materials. Commerical 1,2-dicyanobenzene (Tokyo Kasei, G. R.) was purified by recrystallization from benzene and acetone solutions, and then by fractional sublimation *in vacuo* (0.1 Pa). Orthorhombic and monoclinic crystals are known for this compound,[4,5] though it is not clear which form is more stable. The purified sample showed neither exothermic nor endothermic anomalies between ambient and melting temperatures on DSC curves. In this respect the sample obtained is supposed to be in the stable form. 1,3-Dicyanobenzene supplied from Nihon Shokubai Kagaku Co., Ltd., and commerical 1,4-dicyanobenzene (Nakarai, G. R.) were purified by recrystallization from benzene solution, and subjected to fractional sublimation *in vacuo* (0.1 Pa), and again recrystallization from acetone solution. After brief drying *in vacuo*, a pellet drying procedure[31,32] was applied for the samples. A small endothermic peak with complicated shape was observed at *ca.* 430 K in every DSC heating curve of the latter compound, but the anomaly was not studied in further detail. Purity assessment for the three samples by DSC continuous method gave values higher than 99.9%.

Combustion Calorimetry. A rotating bomb calorimeter of isoperibol type with a platinum-lined bomb, described elsewhere,[6] was used in this study without rotating the bomb. The calorimeter was calibrated with the United States National Bureau of Standards S. R. M. 39i benzoic acid . The mean and standard deviation of mean for energy equivalents of the standard calorimetric system from six calibration experiments were $(15164.84\pm0.53)\ \mathrm{J\ K^{-1}}$.

The dicyanobenzenes are as volatile as may be purified by vacuum sublimation. However, no significant loss in mass was observed for pellets of the compounds each weighing about 1 g, when placed in air at ambient temperatures for several hours. All the combustion experiments were, therefore, carried out without enclosing the samples. An ordinary platinum crucible weighing 11.1 g was used to burn pellets of the compounds. In some of the experiments on 1,4-dicyanobenzene a deep platinum crucible with a baffle (total mass: 29.5 g) described previously[7] was employed, since the pellets showed some tendency of explosion to get out of the open crucible when partially burnt.

In order to determine a small amount of nitric acid produced as a by-product of combustion, the internal space of the bomb was washed with distilled water and the washings were adjusted to 100 cm^3. The nitric acid in the washings was titrated potentiometrically with sodium hydroxide solution, which in turn was standardized with potassium dihydrogenphosphate. Nitric acid formed in the calibration experiments was determined spectrophotometrically by using a UV absorption band

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[††] Debye $=3.333\times10^{-30}$ cm.

TABLE 1. AUXILIARY DATA FOR THE CALCULATION OF STANDARD ENERGY OF COMBUSTION

		ρ/g cm^{-3}	c_p/J K^{-1} g^{-1}	$(\partial E/\partial p)_T$/J MPa^{-1} g^{-1}
1,2-Dicyanobenzene	$C_8H_4N_2$	1.24	(1.19)	(−0.12)
1,3-Dicyanobenzene	$C_8H_4N_2$	1.26	(1.19)	(−0.12)
1,4-Dicyanobenzene	$C_8H_4N_2$	1.29	(1.19)	(−0.12)
Fuse	$CH_{1.860}O_{0.930}$	1.5	1.70	(−0.287)

T_h=298.15 K, V(bomb)=0.3469 dm^3, $\Delta E_c^\circ/M$(fuse)=−16507 J g^{-1}

at 202 nm.

Measurement of Temperature Dependence of Vapor Pressure. The vapor pressures of the samples were measured relatively with a DuPont Model 916 Thermal Evolution Analyzer, which was used in conjunction with a DuPont 990 Thermal Analysis System. It is based on the gas-saturation method and a flame ionization detector (F. I. D.) is used for quantitative determination of a small amount of organic species effused from the Knudsen type cell to carrier gas.[8] Increase h in the F. I. D. current caused by saturation of the carrier gas with the effused organic vapor was measured as a function of temperature. The quantity h is taken to be proportional with the saturation vapor pressure of the compound. Details of the experimental procedures were described elsewhere.[9]

Auxiliary Quantities. The experimental results were based on relative atomic weights recommended by IUPAC Commission on Atomic Weights (1970). The data of density ρ, specific heat capacity c_p, and compression energy $(\partial E/\partial p)_T$ at 298.15 K used for reduction to the standard state and for correction of weights in air to masses are shown in Table 1. The densities of the dicyanobenzenes given in Table 1 were determined by measuring the mass of a pellet of measured size as was reported by Good *et al.*[10] The procedure was examined for benzoic acid. The derived density (1.32 g cm^{-3}) agreed well with a literature value.[30] The densities thus determined were in fair agreement with the values obtained by X-ray method: 1.25 and 1.21 g cm^{-3} for orthorhomboic[4] and monoclinic[5] forms of the 1,2-isomer, respectively, and 1.283 g cm^{-3} for the 1,4-isomer.[20]

The specific heat capacities and compression energies for the dicyanobenzenes given in Table 1 are estimated values. Other auxiliary quantities used in the calculation are also collected in the table. Uncertainties given in this paper are uncertainty intervals defined by Rossini,[33] *i. e.* twice the final overall standard deviation of mean, unless otherwise stated.

Results

Standard Energies of Combustion. Six combustion experiments were carried out for 1,2- and 1,3-dicyanobenzenes, respectively. Eight combustion experiments were carried out for 1,4-dicyanobenzene, among which the deep crucible with a baffle was employed for six samples. The idealized combustion reaction at 298.15 K, to which standard energies and enthalpies of combustion refer, is expressed by the following equation:

$$C_8H_4N_2(c) + 9O_2(g) = 8CO_2(g) + 2H_2O(l) + N_2(g).$$

Results of typical combustion experiments are shown in Table 2. Symbols used in the table are similar to those used by Hubbard *et al.*[12] except for ΔE (std. state), which is the sum of items 81—85 and 87—94 as defined by Hubbard *et al.*[12] Six derived standard energies of combustion ΔE_c°/kJ mol^{-1} for 1,2-dicyanobenzene were −4000.12, −4000.36, −3999.52, −4000.08, −4001.44, and −4000.65, respectively, and mean and standard deviation of mean was −(4000.36±0.26). For 1,3-dicyanobenzene, they were −3991.43, −3991.88, −3991.60, −3992.73, −3992.66, and −3993.41, and mean and standard deviation of mean was found to be −(3992.28±0.31). For 1,4-dicyanobenzene, they were −3988.61, −3988.23, −3987.35, −3988.59, −3988.73, −3987.88, −3987.72, and −3987.23, of which the latter six were obtained by using the deep crucible with a baffle. Mean and standard deviation of mean were −(3988.42±0.19) for

TABLE 2. RESULTS OF TYPICAL COMBUSTION EXPERIMENTS

Dicyanobenzene	1,2-[a]	1,3-[a]	1,4-[a]	1,4-[b]
m^i(compd)/g	0.88438	0.87325	0.87357	0.87796
m^i(fuse)/g	0.00259	0.00257	0.00296	0.00306
m^i(H_2O, tot.)/g	1.1717	1.1527	1.1527	1.1629
p^i(gas)/MPa	3.040	3.059	3.039	3.041
θ_i/°C	23.163198	23.146460	23.156930	23.106719
θ_f/°C	25.016991	24.975439	24.983694	24.943305
$\Delta\theta_{corr}$/°C	0.026023	0.027873	0.026284	0.030085
n^f(HNO_3)/mmol	1.229	1.236	1.180	0.631
ΔE_{ign}/J	6.7	7.3	6.9	7.4
ε^i(cont.)/J K^{-1}	17.8	17.8	17.7	20.4
ε^f(cont.)/J K^{-1}	18.1	18.1	18.1	20.9
$\Delta E_{decomp.}$(HNO_3)/J	72.4	72.8	69.5	37.2
ΔE(std. state)/J	90.5	90.8	87.2	54.8
$\Delta E_{I.B.P.}$/J	−27743.8	−27338.4	−27329.1	−27425.4
ΔE_c°/kJ mol^{-1}	−4000.36	−3991.88	−3988.61	−3987.23

a) The sample was burnt in an open crucible weighing 11.1 g. b) The sample was burnt in a deep crucible with a baffle (total mass: 29.5 g).

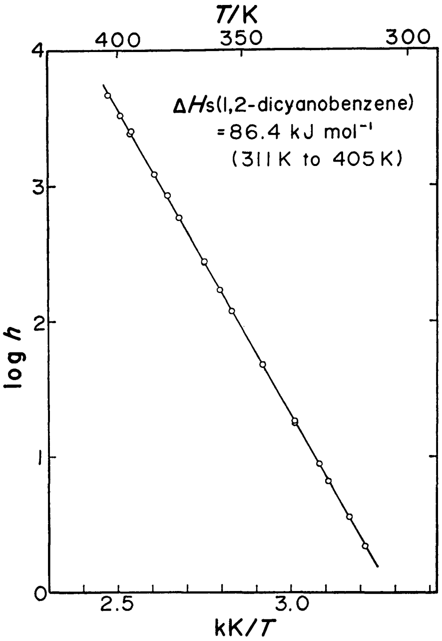


Fig. 1. Temperature dependence of vapor pressure of 1,2-dicyanobenzene. The quantity *h* is proportional to saturation vapor pressure of the compound and is given in arbitrary unit.

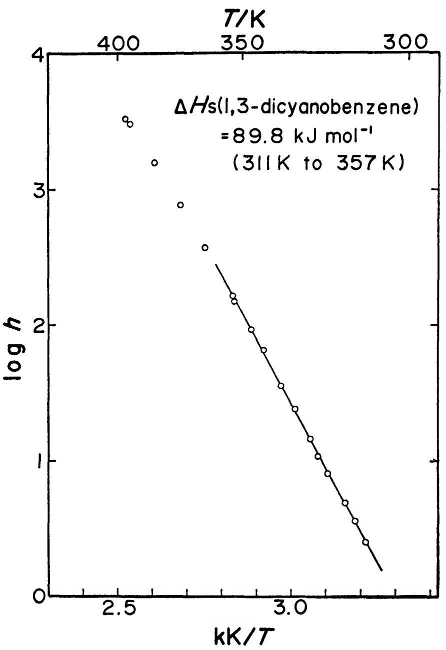


Fig. 2. Temperature dependence of vapor pressure of 1,3-dicyanobenzene. The quantity *h* is proportional to saturation vapor pressure of the compound and is given in arbitrary unit.

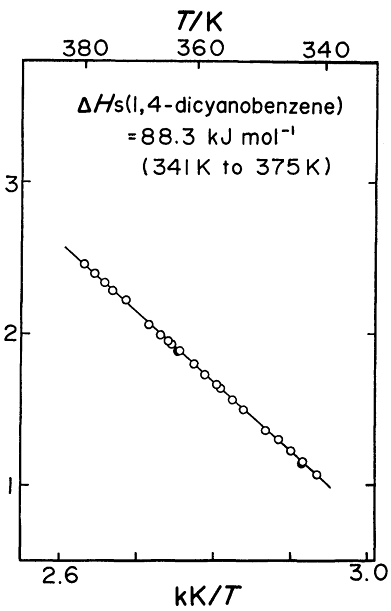


Fig. 3. Temperature dependence of vapor pressure of 1,4-dicyanobenzene. The quanitty *h* is proportional to saturation vapor pressure of the compound and is given in arbitrary unit.

the former two and $-(3987.92\pm0.58)$ kJ mol^{-1} for the latter six experiments, respectively. In spite of difference in the mass of crucible and the amount of nitric acid formed between these kinds of experiments, the discrepancy of the derived enthalpies of combustion was not significant. Hence, the final mean and standard deviation of mean for 1,4-dicyanobenzene were calculated for all of the combustion experiments as follows: ΔE_c°/kJ mol^{-1} $= -(3988.04\pm0.21)$.

Enthalpies of Sublimation. Plots of log *h* against T^{-1} are given in Figs. 1, 2, and 3 for 1,2-, 1,3-, and 1,4-dicyanobenzenes, respectively. With a least squares method, the plots were fitted to straight lines and enthalpies of sublimation at mean temperatures were calculated from the slope of the straight lines on the basis of Clausius-Clapeyron equation. Vapor pressures are so low in the experimental temperature ranges that the enthalpies of sublimation were taken to be standard enthalpies of sublimation. The derived standard enthalpies of sublimation ΔH_s°/kJ mol^{-1} and mean temperatures T_m/K are as follows: 86.4 ± 1.5, 358 for 1,2-dicyanobenzene; 89.8 ± 1.5, 334 for 1,3-dicyanobenzene; 88.3 ± 1.5, 358 for 1,4-dicyanobenzene, respectively, where uncertainties are estimated values. Reduction of the standard enthalpies of sublimation at the mean temperatures to those at 298.15K were performed by estimating molar heat capacities common to three

TABLE 3. DERIVED STANDARD THERMODYNAMIC QUANTITIES AT 298.15 K FOR DICYANOBENZENES

Compound	$-\Delta E_c^\circ$(c) $= -\Delta H_c^\circ$(c) / kJ mol^{-1}	ΔH_f°(c) / kJ mol^{-1}	ΔH_s° / kJ mol^{-1}	ΔH_f°(g) / kJ mol^{-1}
1,2-Dicyanobenzene	4000.36 ± 0.67	280.62 ± 1.23	86.9 ± 1.5	367.5 ± 1.9
1,3-Dicyanobenzene	3992.29 ± 0.75	272.55 ± 1.28	90.1 ± 1.5	362.7 ± 2.0
1,4-Dicyanobenzene	3988.04 ± 0.59	268.30 ± 1.19	88.8 ± 1.5	357.1 ± 1.9

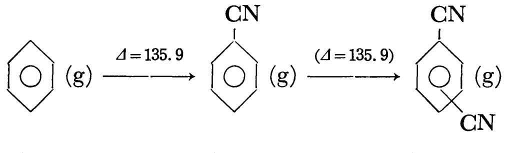
dicyanobenzenes in gaseous and crystalline states. For gaseous state group contributions given by Benson *et al.*[13] were used and for crystalline state specific heat capacities were assumed to be given by the following expression: c_p/J K^{-1} g^{-1}=1.10+0.0035 (T—298.15). The corrections amounted to +0.5, +0.3 and +0.5 kJ mol^{-1} for 1,2-, 1,3-, and 1,4-dicyanobenzenes, respectively.

Derived Thermodynamic Quantities. In Table 3 are given the standard energies of combustion ΔE_c°(c) and standard enthalpies of combustion ΔH_c°(c) determined for three dicyanobenzenes together with standard enthalpies of sublimation ΔH_s° and derived standard enthalpies of formation of crystalline state ΔH_f°(c) and of gaseous state ΔH_f°(g) at 298.15 K. ICSU-CODATA key values[14] for standard enthalpies of formation of CO_2(g) and H_2O(l) were employed to calculate the standard enthalpies of formation in crystalline state.

Discussion

Comparison with Literature Values. No thermochemical determinations have been reported so far for 1,2-, 1,3-, and 1,4-dicyanobenzenes, except for the combustion calorimetric result of Salley and Gray[15] for the 1,2-isomer. The reported standard enthalpy of combustion, corrected for molar atomic masses and density, is −3995.49±1.00 kJ mol^{-1}, which is well outside the uncertainty interval of the present result, the difference being *ca.* 0.125% of the total. The calorimetric sample of Salley and Gray had been purified by recrystallization of a commercial sample from ethanol solution and had a melting point of 411.7—413.2 K. The observed nitrogen content was 99.0% of the theoretical. They stated that the accuracy of their value was almost certainly poorer than the precision (*e.g.*, 0.025% for 1,2-dicyanobenzene) of determinations, since the purity of the sample was the limiting factor.[15] In addition, 1,2-dicyanobenzene was not included in their list of compounds which was considered to be relatively pure.

Estimation of Destabilization Energies. The increment of intramolecular energy which is accompanied by the substitution of one cyano group to a benzene ring was evaluated as the difference (Δ=+135.9 kJ mol^{-1}) between the enthalpy of formation in gaseous state ΔH_f°(g) of cyanobenzene[16] and that of benzene,[17] as illustrated below:

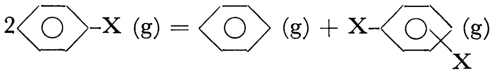


$\frac{\Delta H_f^\circ(g)}{\text{kJ mol}^{-1}}$: 82.9 218.8 (354.7)

If the increment, 135.9 kJ mol^{-1}, were assumed to be transferable to the substitution of the second cyano group, the standard enthalpy of formation in gaseous state of dicyanobenzene would be 354.7 kJ mol^{-1} as shown above. This value may be taken to be the standard enthalpy of formation in gaseous state of hypothetical "non-destabilized" dicyanobenzene. Comparison of the experimental values with this value gave destabilization energies of 12.8±1.9, 8.0±2.0, and 2.4±1.9 kJ mol^{-1} for 1,2-, 1,3- and 1,4-dicyanobenzenes, respectively.[†††] Among them, the 1,4-isomer is most stable and barely destabilized, the 1,3-isomer is intermediate and the 1,2-isomer is least stable. In this scheme, contributions from interactions between a benzene ring and a cyano group is eliminated automatically. Hence, the destabilization energies thus calculated are related only with interactions between the cyano-substituents.

TABLE 4. DESTABILIZATION ENERGIES E_{destab} OF DI-SUBSTITUTED BENZENES

The energies were calculated as enthalpy changes for the following hypothetical reactions:



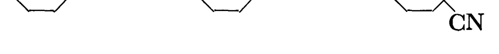
Isomer	E_{destab}/kJ mol^{-1}		
X=	F	Cl	CN
1,2-	21.2	10.4	12.8
1,3-	5.7	6.2	8.0
1,4-	8.4	2.9	2.4

Destabilization energies calculated similarly for difluoro- and dichlorobenzenes[17] were compared with those of dicyanobenzenes in Table 4. Destabilization energy of dicyanobenzene are of similar magnitude to that of the corresponding dichlorobenzene and lower than that of the corresponding difluorobenzene. It is worth noting that for difluorobenzene the 1,3-isomer is more stable than the 1,4-isomer in contrast to the trend found in dichloro- and dicyanobenzenes. Niessen[18] made *ab initio* MO calculations to obtain total energies of disubstituted benzenes including difluoro- and dicyanobenzenes. In all cases, the total energies were found to increase in the sequence of 1,3-, 1,4-, and 1,2-isomers in accordance with the trend experimentally found for difluorobenzenes. However, the differences in the total energies between 1,4- and 1,3-isomers and between 1,2- and 1,3-isomers obtained by Niessen were 0.67 and 2.72 kJ mol^{-1} for dicyanobenzenes, respectively, and 62.9 and 95.4 kJ mol^{-1} for difluorobenzenes, respectively. The latter differences are too large as compared with thermochemical values.

Interpretation of Destabilization Energies. The molecular structure of cyanobenzene was determined by Bak *et al.* from microwave spectroscopy.[19] The C–C distance of benzene is practically conserved in the structure. Changes of valence angles are definitely present, but are small (0—2.5°). The C–CN and C–N distances are 0.1455(7) and 0.1159(2) nm, respectively, where numbers in parentheses are estimated uncertainties for the final significant figures. The cyano group is coplanar with the benzene ring.

The molecular and crystal structures of 1,4-dicyano-

[†††] The destabilization energies are equivalent to enthalpy changes for the following hypothetical reactions:



benzene were determined by van Rij and Britton[20]) from X-ray diffraction method. The C–C distances in the benzene ring are all normal. The C–CN and C–N distances are 0.1438(3) and 0.1147(4) nm, respectively, where numbers in parentheses are estimated standard deviations expressed in the same way as above. The cyano groups deviated from coplanarity significantly, but slightly. 1,2-Dicyanobenzene crystallizes in two forms: orthorhombic[4]) and monoclinic.[5]) X-ray diffraction studies on these crystals indicated that the bond distances in the molecule are almost equal to the corresponding ones in a 1,4-dicyanobenzene molecule and the cyano groups are almost coplanar with the benzene ring.[4,5]) No structural determinations have been reported for 1,3-dicyanobenzene.

These facts show that no remarkable difference in corresponding molecular parameters are observed among cyanobenzene and 1,2- and 1,4-dicyanobenzenes. It seems likely that the same would hold for 1,3-dicyanobenzene. These statements may be part of the reasonings which support the estimation of distabilization energies between substituents based on the scheme described above.

The dipole moment of a free cyanobenzene molecule is 4.14 Debye, which has been determined by Lide from microwave spectroscopy.[21]) Charge distribution and dipole moment of a cyanobenzene molecule in the ground state have been studied by using molecular orbital methods of various levels. At the level of semi-empirical all valence electron MO methods, King and van Putten[22]) calculated charge densities on all the atoms of the molecule (CNDO/CI method) and Klasing *et al.*[23]) calculated charge densities on carbon and nitrogen atoms (CNDO/2 method). Charge densities on cyano carbon and nitrogen atoms and negative charge donated from the benzene ring to the substituent were calculated to be $+0.090e$, $-0.212e$, and $-0.122e$ by King and van Putten[22]) and $+0.089e$, $-0.166e$, and $-0.077e$ by Klasing *et al.*,[23]) respectively. Bloor and Breen[24]) used a CNDO/2 method to calculate contributions to total dipole moment from atomic charge densities (p^σ and p^π, where σ and π denote σ and π electrons, respectively) and from the atomic dipole moment(p_{sp}) arising from the mixing of the s and p orbitals on the same atom and including lone-pair moment of the hetero-atom. The derived results were as follows: $p^\sigma=0.25$, $p^\pi=1.52$ and $p_{\mathrm{sp}}=1.45$ Debye and total dipole moment was 3.23 Debye. At the level of *ab initio* MO method, Hehre *et al.*[25]) made a calculation with the minimal STO-3G basis set to determine the total dipole moment p and total σ and π charges, q^σ and q^π, donated from the benzene ring to the substituent. Derived results were as follows: $p=3.65$ Debye, $q^\sigma=-0.104e$, and $q^\pi=-0.022e$.

As described in Appendix, the dipole moments of 1,2- and 1,3-dicyanobenzenes in benzene solution amount to *ca.* 95% of the values calculated as vector sum of the dipole moment of cyanobenzene in benzene solution and that of the 1,4-isomer is, at least, nearly equal to zero. The dipole moments in dioxane solution showed similar tendency. The charge distribution in the cyano groups of dicyanobenzene molecules is considered to be similar to that in the molecules of cyanobenzene. This is another reasoning to support the use of the scheme described above to obtain destabilization energies.

Although the destabilization of 1,2-dialkylbenzene may be ascribed to repulsive interaction between buttressed alkyl groups, that of 1,2-dicyanobenzene may hardly be due to the same cause. The molecular orbital calculations did not reproduce exactly the experimental total permanent dipole moment of 4.14 Debye, but indicated that the dipole moment of cyanobenzene comes from (1) net charge donated from the benzene ring to the substituent, (2) polarization of the C–N bond and (3) lone pair electrons on the nitrogen atom. Hence, the destabilization in the dicyanobenzenes is most likely to be due to electrostatic interactions between the substituents.

The validity of the inference may be shown by the calculation described below. For simplicity, the electrostatic interaction is assumed to be represented by dipole-dipole interaction between electric dipoles located at the positions of nitrogen atoms. Interaction energy E_{el} between two electric dipoles with moments μ_1 and μ_2, respectively, is expressed by the following equation:

$$E_{\mathrm{el}} = \frac{\mu_1\mu_2}{r_{12}^3}(3\cos\theta_1\cos\theta_2 - \cos^2\theta_{12}), \qquad (1)$$

where, r_{12} is the distance between the dipoles, θ_1 and θ_2 are the inclination angles of them to the line of centers, and θ_{12} is the angle between them.

If the dipole-dipole interaction energy and the thermochemical destabilization energy for 1,2-dicyanobenzene (12.8 kJ mol^{-1}) are equated, the dipole moment of 3.27 Debye is derived. Use of this value together with equation (1) leads in turn to dipole-dipole interaction energies of 4.3 and 2.6 kJ mol^{-1} for 1,3- and 1,4-dicyanobenzenes, respectively. In this calculation the following assumptions were made of the molecular structure of the dicyanobenzenes: (i) C–C–N moiety is linear, (ii) the molecules are planar including the substituents, (iii) C–CN and C–N distances are transferable between 1,4-dicyanobenzene and both of the 1,2- and 1,3-isomer; the reported values for the 1,4-isomer[20]) were used in common, and (iv) benzene rings are regular hexagons with C–C distances of 0.1393 nm.

The derived dipole moment, 3.27 Debye, is considered to be of reasonable magnitude in view of the observed dipole moments of the dicyanobenzenes in benzene and dioxane solutions and also the result of the MO calculations on cyanobenzene. The magnitude of the calculated dipole-dipole interaction energies for 1,3- and 1,4-dicyanobenzenes are comparable with the thermochemical destabilization energies. Thus, experimental results from thermochemical and dielectric measurements have been interpreted consistently on the basis of the single model. Accordingly, it may be concluded that electrostatic interactions between the cyano substituents on one and the same benzene ring are responsible for the destabilization observed for the molecules of 1,2-, 1,3-, and 1,4-dicyanobenzenes.

The authors are indebted to Mr. Keiichi Nishiyama and Mr. Junichi Furukawa, who assisted the determinations of enthalpies of sublimation and of dipole moments, respectively. They also thank Professor Doyle Britton of University of Minnesota, Professor Kenji Osaki and Dr. Tsuneyuki Higashi of Kyoto University, and Dr. Noritake Yasuoka and Mr. Atsushi Kume of Osaka University for communicating the results of X-ray diffraction studies prior to publication and Nihon Shokubai Kagaku Co., Ltd. for their kind supply of dicyanobenzenes.

Appendix

Dipole Moments in Solution of 1,2-, 1,3-, and 1,4-Dicyanobenzenes. Dielectric constant and refractive index were measured at 298.15 K for the benzene and dioxane solutions of the dicyanobenzenes in the range up to 0.15 mol dm^{-3}. The cell used for the dielectric measurement was similar to that described by Hassion and Cole.[26] Dielectric constant was measured at 1 kHz with a General Radio Type 1615 Capacitance Bridge.

Dipole moment, p, was calculated on the basis of the Guggenheim's equation:[27]

$$\left(\frac{p}{\text{Debye}}\right)^2 = \frac{9\times10^{36}kT}{4\pi N_\text{A}}\,\frac{3}{(\varepsilon_1+2)(n_1{}^2+2)} \times\left[\frac{(\varepsilon_{12}-n_{12}^2)-(\varepsilon_1-n_1{}^2)}{(c/\text{mol dm}^{-3})}\right]_{c\to0},$$

where ε_1 and ε_{12} are the dielectric constants of the solvent and solution, respectively, and n_1 and n_{12} are the refractive indices of the solvent and solution, respectively; c is the concentration, k the Boltzmann constant, and N_A the Avogadro constant. In Table 5, the derived dipole moments are presented and compared with the calculated values for benzene solutions, which were obtained as the vector sums of the dipole moment of cyanobenzene in benzene solution.[28,29]

Table 5. Dipole moment p in benzene and dioxane solutions of 1,2-, 1,3-, and 1,4-dicyanobenzenes

Compound	p/Debye[a)]		
	In benzene		In dioxane
	Exptl	Calcd	Exptl
Cyanobenzene	4.05[c)]	4.05	
1,2-Dicyanobenzene	6.57	7.00	6.82
1,3-Dicyanobenzene	3.86	4.05	3.99
1,4-Dicyanobenzene	——[b)]	0	——[b)]

a) Debye/C m$=3.333\times10^{-30}$. b) The value is small and not significant. c) Refs. 28 and 29.

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