Experimental Assessment of the Effect of a Bicyclo[1.1.0]butane System in Strain-Induced Localisation of Aromatic π-Bonds

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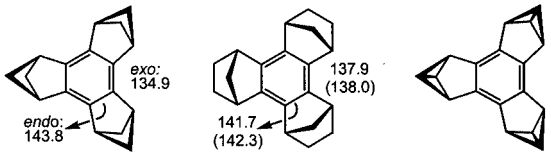
The geometrical parameters of the dimethyl pyridazine-1,4-dicarboxylates **13**–**16**, in which a σ-bond system is annulated at the C5–C6 bond, have been determined by X-ray diffraction. As compared to the cyclopentene subunit in **16**, which is believed to exert no significant influence on the bond lengths of the aromatic moiety, the norbornene, benzvalene, and bicyclo[2.1.1]hexene subunits of **13**–**15**, respectively, cause alternating bond elongations and shortenings in the pyridazine moiety, with increasing magnitudes, in that order. These effects are in line with the heats of the isodesmic reactions that convert norbornene (**8**), benzvalene (**6**), and bicyclo[2.1.1]hex-2-ene (**4**) with buta-1,3-diene into ethene as well as 2,3-bis(methylene)norbornane (**9**), 3,4-bis(methylene)-tricyclo[3.1.0.0^{2,6}]hexane (**7**), and 2,3-bis(methylene)bicyclo[2.1.1]hexane (**5**), respectively. Calculated originally by W. L. Jorgensen and W. T. Borden in the 1970s, the reactions have now been reexamined by employing much higher levels of theory.

Introduction

By the synthesis[1] and the determination of the geometrical parameters[2] of the trimethanotrindene **1**, Siegel et al. have demonstrated that the annulation of strained σ-bond systems can cause an impressive bond localisation in the benzene subunit (Scheme 1). Even if the effect is smaller, the replacement of the four-membered rings of **1** by five-membered ones, as in **2**, still brings about a significant bond length alternation (Scheme 1).[3,4] A number of compounds related to **2**, in which the cyclopentane moieties are formally substituted by units derived from indane, cyclopentene, 2,5-dihydrofuran, cyclohexane, or 9,10-dihydroanthracene, have been examined with respect to bond fixation.[5]



Scheme 1. Benzenes with annulated σ-bond systems; in the case of the known compounds **1** and **2**, the bond lengths [pm] of the benzene nucleus are those of ref.[2] (**1**), ref.[3] (**2**), and ref.[4] (**2**, values in parentheses)

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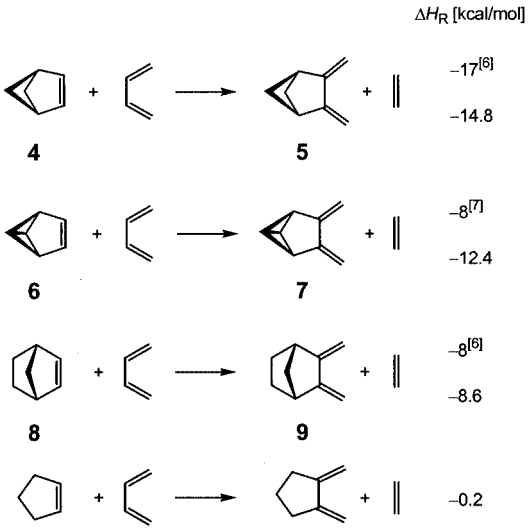
A substantial enhancement of the strain energy in the annulated σ-bond system is conceivable by introduction of a bicyclo[1.1.0]butane skeleton as in **3** (Scheme 1). Since **3** has not yet been synthesised, we report herein the experimental determination of the detailed structure of the pyridazines **13**−**15**. Although only one σ-bond system is annulated to the aromatic nucleus, the effect of the cyclobutane, bicyclobutane, or cyclopentane unit is clearly discernible so that the bond lengths of **3** can be estimated reliably relative to those of **1** and **2**.

Results and Discussion

1. Isodesmic Reactions of Bicyclo[2.1.1]hex-2-ene (4), Benzvalene (6), and Norbornene (8) in Accordance with Jorgensen and Borden[6,7]

Contrary to the intuition that greater strain will induce a more extensive localisation of aromatic π-bonds, Jorgensen and Borden predicted as early as in the seventies that the bicyclobutane system[7] will be less efficient than a cyclobutane moiety.[6] This estimation was based on the heats of the isodesmic reactions shown in Scheme 2, which were calculated by using the extended Hückel method. Accordingly, the conversion of bicyclo[2.1.1]hex-2-ene (**4**) with buta-1,3-diene into ethene and 2,3-bis(methylene)bicyclo[2.1.1]hex-

ane (**5**) was found to be exothermic by 17 kcal/mol,[6] whereas the analogous process of benzvalene (**6**) resulting in **7** should furnish only 8 kcal/mol,[7] just as much as the transformation of norbornene (**8**) to 2,3-bis(methylene)norbornane (**9**).[6]

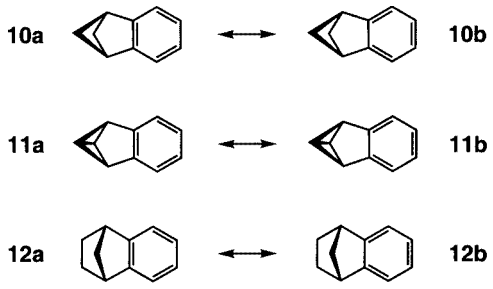


Scheme 2. Heats of the isodesmic reactions of *cisoid*-buta-1,3-diene with bicyclo[2.1.1]hex-2-ene (**4**), benzvalene (**6**), norbornene (**8**), and cyclopentene with formation of ethene and the 2,3-bridged buta-1,3-dienes **5**, **7**, **9**, or 1,2-bis(methylene)cyclopentane, respectively; the upper values were obtained by Jorgensen and Borden (refs.[6,7]) employing extended Hückel calculations; the lower values have been determined in the present work by using a CCSD(T)/cc-pVDZ procedure; the energetics of the conversion of cyclopentene were obtained by using the DFT method

Computational methods have improved dramatically since the 1970s, which is why we have reanalysed the reactions of Scheme 2 performing DFT [B3LYP/6-31G(d)] and Coupled Cluster calculations [CCSD(T)/*cc*-pVDZ]. Both procedures gave similar results, of which only those of the latter one are presented in Scheme 2. Akin to the previous outcome,[6,7] the heat of the norbornene (**8**) reaction (−8.6 kcal/mol) amounts to somewhat more than half the value of that of bicyclo[2.1.1]hex-2-ene (**4**, −14.8 kcal/mol). The benzvalene (**6**) reaction, however, turned out to be significantly more exothermic (−12.4 kcal/mol) than computed earlier.[7] In the case of the reaction of **6**, a CCSD(T)/*cc*-pVTZ calculation has been performed with virtually the same outcome (−12.8 kcal/mol). Thus, the effect of the bicyclobutane system is inferior to that of a cyclobutane moiety by only 2.4 kcal/mol. As a reference system, we have added in Scheme 2 the corresponding conversion of cyclopentene into 1,2-bis(methylene)cyclopentane, which was calculated to be virtually thermoneutral (−0.2 kcal/mol).

The analysis of the photoelectron spectra of **4**−**7** has revealed that the bicyclobutane subunit interacts considerably more strongly with the π-systems than the cyclobutane entity. Within a ZDO model, the resonance integrals β amount to −2.3 (**6**, **7**) and −1.9 eV (**4**, **5**), respectively.[8] Obviously, cyclobutane must be much more strongly biased, as compared to bicyclobutane, toward bridging butadiene across the C2−C3 bond and against bridging ethene and, thus, can overcompensate the effect of the resonance integrals, resulting in the greatest exothermicity of its isodesmic reaction in Scheme 2.

The transfer of the energetics of Scheme 2 to **10**−**12**, the benzannulated derivatives of **4**, **6**, and **8**, leads to the inequality of the two Kekulé structures. Accordingly, **10a**, **11a**, and **12a** should contribute less to the ground state of the hydrocarbons than **10b**, **11b**, and **12b**. Consequently, the benzene subunits of **10**−**12** should exhibit a bond alternation with the π-bonds preferably localised as in **10b**, **11b**, and **12b**, and the largest effect has to be expected in the case of **10**, and the smallest in the case of **12**. Three σ-systems at one benzene nucleus as in **1**−**3** should cumulatively act causing the bond length differences of ca. 9 and ca. 4 pm in **1** and **2**, respectively (Scheme 1). On the basis of the computational results depicted in Scheme 2, a bond length difference of ca. 7 pm can be predicted for **3**.

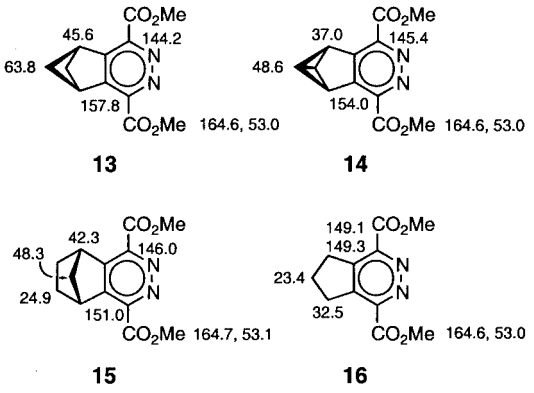


Scheme 3. Kekulé structures of 2,3-dihydro-1*H*-1,3-methanoindene (**10**), 2,3-dihydro-1*H*-1,2,3-methenoindene (**11**), and 1,2,3,4-tetrahydro-1,4-methanonaphthalene (**12**)

2. An Experimental Test for the Effect of the σ-Bond Systems in 10−12 with the Structural Parameters of the Pyridazine Derivatives 13−16

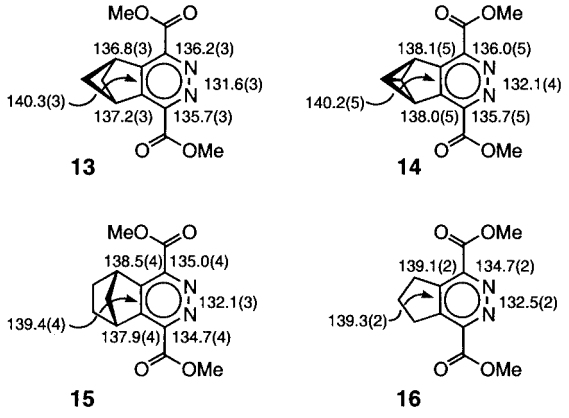
Compounds **10**−**12** are well known, but our attempts to grow a single crystal of **11**, which is a liquid at room temperature, failed. Unlike **11**, the pyridazine-1,4-dicarboxylates **14**[9] and **16**[10] (Scheme 4) are well-crystallising solids, which can be prepared readily from benzvalene (**6**) and cyclopentene, respectively, by reaction with dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate. Analogously, we obtained **13** and **15** (Scheme 4) starting from **4** and **8**. In the latter case, the isolation of two dihydro derivatives of **15**, which only had to be dehydrogenated, was described previously.[11] We took **16** as a reference compound, in which the bond lengths in the aromatic nucleus should be essentially unaffected by the annulated five-membered ring.

The ^{13}C NMR chemical shifts are highly characteristic for **13**−**16** (Scheme 4). Of particular interest are the signals of the pyridazine nuclei, which display almost no difference ($\Delta\delta$ = 0.2 ppm) in **16**, but differ by 5.0 ppm in **15**, by 8.6 ppm in **14**, and 13.6 ppm in **13**. As will be shown below, the difference in the lengths of the two types of C−C bonds in the pyridazine subunit increases in the same sequence.



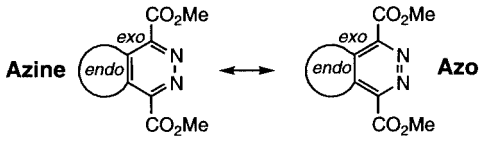
Scheme 4. ^{13}C NMR chemical shifts (δ values, $CDCl_3$) of the pyridazine-1,4-dicarboxylates **13**−**16**; the assignment of the signals to the carbon atoms of the pyridazine subunit is based on a proton-coupled spectrum of **13** and was transferred accordingly to **14** (ref.[9]) and **15**

The structures of **13**[12] and **14**[13] have been determined previously at room temperature, but we repeated the experiments at −80 °C to obtain comparable data for the whole set. For the discussion of small geometrical trends, low-temperature data are much more reliable as the experimental standard deviations tend to be lower. Scheme 5 contains the bond lengths of the pyridazine subunits of **13**−**16**. The formulae represent the positions of the atoms in an approximately correct manner, although a drawback of analysing **13**−**15**, as compared to the hydrocarbons **10**−**12**, becomes obvious: the dissimilar arrangement of the ester groups. They are coplanar with the aromatic nucleus or almost so (dihedral angles in **13**: 0°; in **14**: 12.3 and 16.1°; in **15**: 13.8 and 4.7°; in **16**: 0.7°), but the conformation differs as it is transoid in **13** and **15** and cisoid in **14** and **16**. This variation could influence the bond lengths slightly in the pyridazine subunit. Thus, the following discussion is tainted with this possibility.



Scheme 5. Bond lengths [pm] of the aromatic moieties of the pyridazine-1,4-dicarboxylates **13**−**16** as determined by X-ray diffraction; the error limit is given in brackets and refers to the figure after the decimal point

Even if the differences in the bond lengths of the aromatic moieties between next neighbours in the series **13**−**16** are small, and in some instances within the error limit, significant effects become evident on comparison of **13** with **16**. Whereas the lengths of both types of C−C bonds in **16** are virtually equal, the bond bridged by the σ-system (*endo*) is longer by 3.3 pm than the other C−C bonds (*exo*) in **13**. Similarly, the lengths difference between the N−N bond and the C−N bonds increases from 2.2 pm in **16** to 4.4 pm in **13**. These variations indicate a change in the contributions of the Kekulé structures **Azine** and **Azo** (Scheme 6) to the ground state of **13**−**16**, with the weight of **Azo** being greater in the case of **13** as compared with **16**. As the bond lengths demonstrate, this variation occurs step by step on going from **16** via **15** and **14** to **13**. Thus, the effects are at least qualitatively in line with the heats of the isodesmic reactions of Scheme 2.



Scheme 6. Kekulé structures of the pyridazine-1,4-carboxylates **13**−**16**

Recently, Shaik et al.[14] have carried out a thorough analysis of the bond length alternation in **1** based on a detailed description of benzene using the valence bond view. Accordingly, the D_{6h} symmetry of benzene is enforced by the σ-bonds, which overcompensate the tendency of the π-electrons to be localised (π-distortivity). Now, the strained σ-systems of **1** have two effects, as they cause an alternation of the σ-bond lengths of the benzene nucleus and an enhancement of the π-distortivity. The former effect was originally advanced by Stanger,[15] who demonstrated that imposing D_{3h} symmetry to benzene by deformation of the C−C−H bond angles leads to an elongation of the C−C bonds being part of the angles < 120° and to a shortening of the other ones. Since the C−C−C bond angles formed by the bridged aromatic bond and the adjacent carbon atoms of the σ-system increase from 102.6° via 105.1° and 106.6° to 111.0° in the series **13**−**16**, the changes of bond lengths correspond to Stanger's prediction. On the other hand, an intense interaction of the pseudo-π-orbitals of the σ-systems with the aromatic π-system is suggested by the photoelectron spectra of **4**−**7**[8] and **11**[16] as well as the energies of the singlet excited states of **11**.[17]

Conclusion

In summary, we have shown that in spite of the high strain energy of the bicyclobutane skeleton, it is, if bridged across positions 2 and 4, inferior to a 1,3-bridged cyclobutane moiety with respect to strain-induced localisation of aromatic π-bonds. It seems that both causes of the phenomenon, as detailed by Shaik et al.,[14] are reliably modelled by the heats of the isodesmic reactions that convert benzvalene (**6**) and bicyclo[2.1.1]hex-2-ene (**4**) with *cisoid*-buta-1,3-diene into ethene as well as 3,4-bis(methylene)tricy-

clo[3.1.0.0^{2,6}]hexane (**7**) and 2,3-bis(methylene)bicyclo-[2.1.1]hexane (**5**), respectively.

Computational Aspects

Geometrical parameters of all stationary points were optimised employing analytic energy gradients within the Density Functional Theory (DFT)[18] approach employing the B3LYP hybrid functional[19,20] in conjunction with the 6-31G(d)[21] basis set. The optimisations were performed without symmetry constraints. All stationary points were analyzed by computed harmonic frequencies on the same level of theory. Vibrational, thermal, and entropy corrections to the energy were computed on the same level of theory at 298 K.[22] All DFT calculations were performed with the Gaussian 98[23] package.

Reaction energies for the isodesmic reactions were obtained also by single-point computations on the optimized stationary points employing the closed-shell Coupled Cluster CCSD(T) ansatz[24−26] in conjunction with a *cc*-pVDZ and a *cc*-pVTZ[27] basis set to evaluate the quality of the DFT calculations. These computations were performed with the MOLPRO 2002.1 package.[28,29] The reliability of the Coupled Cluster ansatz was validated using the T_1 diagnostics. Values of ΔH_{298} for CCSD(T) were computed by adding the thermal corrections obtained with B3LYP/6-31G(d) to the resulting single-point energies.

Supporting Information: Absolute energies and computed structures of all stationary points for compounds **4**−**9** in Cartesian coordinates (PDF) are available free of charge; see footnote on the first page of this article.

Experimental Section

General Remarks: NMR: Bruker AC 200, AC 250, and Avance 400. Internal standards were $CHCl_3$ (δ = 7.26 ppm) or C_6D_5H (δ = 7.15 ppm) for ^{1}H NMR, and $CDCl_3$ (δ = 77.0 ppm) or C_6D_6 (δ = 128.0 ppm) for ^{13}C NMR spectroscopy. The multiplicities of the signals are abbreviated as s (singlet), d (doublet), t (triplet), q (quadruplet), quint (quintuplet), m (multiplet), br (broad), and combinations thereof. A multiplicity in quotation marks indicates a deceptively simple pattern of a higher-order spectrum. Multiplicities in the ^{13}C NMR spectra are given only for those cases for which proton coupling has been determined. Otherwise, the assignment is based on a DEPT sequence or a C,H COSY spectrum. IR: Perkin−Elmer 1420 ratio recording infrared spectrophotometer and 1605 FT-IR spectrometer. MS: Varian MAT CH7 and Finnigan MAT 8200. Elemental analyses: Carlo Erba Strumentatione Elemental Analyzer 1106 and LECO Elemental Analyzer CHNS 932. Melting points: Kofler hot stage from C. Reichert, Optische Werke A. G., Vienna, Austria.

Reaction of Bicyclo[2.1.1]hex-2-ene (4) with Dimethyl 1,2,4,5-Tetrazine-3,6-dicarboxylate (DMTD): Bicyclohexene **4** (85.0 mg, 1.06 mmol) was added dropwise over 5 min to a stirred mixture of DMTD (200 mg, 1.01 mmol) in anhydrous diethyl ether (5 mL) under nitrogen at room temperature. Stirring was continued for 1.5 h, after which time the originally red suspension had turned yellow and the gas evolution had ceased. The precipitate was shown to be dimethyl (4aα,5β,7β,7aα)-5,6,7,7a-tetrahydro-4a*H*-5,7-methanocyclopenta[*d*]pyridazine-1,4-dicarboxylate. Yield: 220 mg (87%), pale yellow crystals, m.p. 78−79 °C. ^{1}H NMR (200 MHz, C_6D_6): δ = 0.40 (dd, J = 10.2, 7.2 Hz, 1 H) and 0.68 (dd, J = 10.2, 8.5 Hz, 1 H) (6,8-H$_{syn}$), 0.92−1.05 (m, 2 H, 6,8-H$_{anti}$), 2.68 (br t, J = 2.5 Hz, 2 H, 5,7-H), 2.71 (br s, 2 H, 4a,7a-H), 3.40 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (50 MHz, C_6D_6): δ = 33.8 and 36.3 (C-6,8), 36.6 (C-5,7), 47.3 (C-4a,7a), 52.2 (CH_3), 158.0 (C-1,4), 165.4 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 1720 cm^{-1} (C=O). MS (70 eV, EI): *m*/*z* (%) = 250 (15) [M$^+$], 191 (100), 133 (58), 131 (26), 104 (27), 79 (57), 77 (42), 59 (70), 39 (28). $C_{12}H_{14}N_2O_4$ (250.3): calcd. C 57.59, H 5.64, N 11.19; found C 57.18, H 5.76, N 10.82.

The solution of the above product in $CDCl_3$ turned colourless within a few days, indicating the complete rearrangement to dimethyl (4aα,5β,7β)-4a,5,6,7-tetrahydro-2*H*-5,7-methanocyclopenta[*d*]pyridazine-1,4-dicarboxylate, m.p. 158−159 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.11 (dd, J = 10.2, 6.9 Hz, 1 H) and 1.68 (dd, J = 10.2, 7.1 Hz, 1 H) (6,8-H$_{syn}$), 2.18−2.28 (m, 2 H, 5,7-H), 2.77 (br s, 1 H, 4a-H), 3.38 (dtd, J = 6.5, 2.8, 1.0 Hz, 1 H, 5-H), 3.66 (dt, J = 6.5, 2.6 Hz, 1 H, 7-H), 3.81 (s, 3 H, CH_3), 3.82 (s, 3 H, CH_3), 8.41 (br s, 1 H, 2-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 39.8 and 41.8 (C-5,7), 43.7 and 46.6 (C-6,8), 45.7 (C-4a), 52.1 (CH_3), 52.2 (CH_3), 121.9 (C-7a), 131.1 and 134.2 (C-1,4), 161.9 (C=O), 164.4 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 1739 cm^{-1} (C=O), 1725 (C=O). MS (70 eV, EI): *m*/*z* (%) = 250 (0.3) [M$^+$], 249 (2), 248 (11), 190 (80), 131 (100), 129 (28), 104 (31), 79 (21), 77 (19), 59 (32), 51 (15), 39 (13). $C_{12}H_{14}N_2O_4$ (250.3): calcd. C 57.59, H 5.64, N 11.19; found C 57.21, H 5.25, N 11.14.

Dimethyl 6,7-Dihydro-5*H*-5,7-methanocyclopenta[*d*]pyridazine-1,4-dicarboxylate (13): Dimethyl (4aα,5β,7β)-4a,5,6,7-tetrahydro-2*H*-5,7-methanocyclopenta[*d*]pyridazine-1,4-dicarboxylate (see above, 180 mg, 0.719 mmol) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 180 mg, 0.793 mmol) were heated under reflux in anhydrous benzene (50 mL) under nitrogen for 15 h. The precipitate formed was removed by filtration and washed with benzene. The filtrate was extracted with aqueous $NaHSO_3$ (38%, 2 × 80 mL) and then with water (100 mL). After having been dried with $MgSO_4$, the benzene solution was concentrated in vacuo. Recrystallisation of the solid residue from ethyl acetate gave pure **13**. Yield: 110 mg (62%), pale yellow plates, m.p. 179−180 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.58 (AA′ part of an AA′MM′X$_2$ spectrum, $J_{A,A'}$ = −10.2, $J_{A,M}$ = −6.8, $J_{A,M'}$ = +0.6 Hz, 2 H, 6,8-H$_{syn}$), 3.00 (MM′ part of an AA′MM′X$_2$ spectrum, J = −10.2, −6.8, +0.6, $J_{M,X}$ = 2.5 Hz, 2 H, 6,8-H$_{anti}$), 3.97 (X$_2$ part of an AA′MM′X$_2$ spectrum, J = 2.5 Hz, 2 H, 5,7-H), 4.06 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 45.6 (ddquint, $J_{C,H}$ = 167, 11, 2 Hz, C-5,7), 53.0 (q, $J_{C,H}$ = 148 Hz, 2 CH_3), 63.6 (dddd, $J_{C,H}$ = 147, 142, 13, 4 Hz, C-6,8), 144.2 (s, C-1,4), 157.8 (“tquint”, line distances 8, 3 Hz, C-4a,8a), 164.6 (q, $J_{C,H}$ = 4 Hz, 2 C=O) ppm. IR (KBr): $\tilde{\nu}$ = 1741 cm^{-1} (C=O), 1720 (C=O). MS (70 eV, EI): *m*/*z* (%) = 248 (13) [M$^+$], 218 (14), 191 (10), 190 (98), 132 (14), 131 (100), 129 (24), 104 (38), 103 (10), 79 (13), 77 (18), 59 (15), 51 (12), 40 (15). $C_{12}H_{12}N_2O_4$ (248.2): calcd. C 58.06, H 4.87, N 11.28; found C 57.86, H 4.85, N 10.96.

Reaction of Norbornene (8) with DMTD: Previously, this reaction was described briefly.[11] We added **8** (100 mg, 1.06 mmol) in small portions to a stirred solution of DMTD (200 mg, 1.01 mmol) in dichloromethane (5 mL) under nitrogen at room temperature. A vigorous evolution of a gas occurred and eventually the solution turned colourless. Removal of the solvent in vacuo and crystallisation of the residue from methanol at −30 °C gave pure dimethyl (4aα,5β,8β)-2,4a,5,6,7,8-hexahydro-5,8-methanophthalazine-1,4-

dicarboxylate. Yield: 210 mg (79%, ref.[11a] 85%), colourless needles, m.p. 122−123 °C (120−121 °C[11a]). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (dquint, *J* = 9.9, 1.9 Hz, 1 H, 9-H$_{syn}$), 1.35 (dddd, *J* = 12.1, 7.6, 3.5, 2.4 Hz, 1 H) and 1.57 (dddd, *J* = 11.6, 7.6, 4.1, 1.9 Hz, 1 H) (6,7-H$_\alpha$), 1.51 (dq, *J* = 9.9, 1.8 Hz, 1 H, 9-H$_{anti}$), 1.79 (tt, *J* = 12.1, 4.3 Hz, 1 H) and 1.86 (tt, *J* = 12.1, 4.0 Hz, 1 H) (6,7-H$_\beta$), 2.10 (d, *J* = 1.8 Hz, 1 H, 4a-H), 3.50 (m, 1 H) and 3.62 (m, 1 H) (5,8-H), 8.52 (br s, 1 H, 2-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 26.2 and 28.9 (C-6,7), 37.5 and 41.3 (C-5,8), 42.2 (C-9), 43.3 (C-4a), 52.20 and 52.22 (2 CH_3), 120.9 (C-8a), 128.6 and 132.2 (C-1,4), 162.0 and 164.1 (2 C=O) ppm; as far as specified, the assignment is based on a C,H COSY spectrum. IR (KBr): $\tilde{\nu}$ = 1713 cm^{-1} (C=O), 1660. MS (70 eV, EI): *m*/*z* (%) = 264 (12) [M$^+$], 249 (12), 224 (13), 223 (100), 205 (12), 191 (40), 79 (13), 65 (12), 59 (18), 40 (19). $C_{13}H_{16}N_2O_4$ (264.3): calcd. C 59.08, H 6.10, N 10.60; found C 58.79, H 6.02, N 10.43.

Dimethyl 5,6,7,8-Tetrahydro-5,8-methanophthalazine-1,4-dicarboxylate (15): Dimethyl (4aα,5β,8β)-2,4a,5,6,7,8-hexahydro-5,8-methanophthalazine-1,4-dicarboxylate (see above, 200 mg, 0.757 mmol) was converted into **15** as described above for the preparation of **13**. Crystallisation of the crude product from methanol (−30 °C) gave pure **15**. Yield: 110 mg (55%), pale yellow needles, m.p. 175−176 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (m, 2 H, 6,7-H$_{endo}$), 1.69 (dt, *J* = 9.8, 1.3 Hz, 1 H, 9-H$_{anti}$), 1.80 (dquint, *J* = 9.8, 1.8 Hz, 1 H, 9-H$_{syn}$), 2.16 (m, 2 H, 6,7-H$_{exo}$), 4.08 (s, 6 H, 2 CH_3), 4.18 (m, 2 H, 5,8-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): Scheme 4. IR (KBr): $\tilde{\nu}$ = 1723 cm^{-1} (C=O). MS (70 eV, EI): *m*/*z* (%) = 262 (6) [M$^+$], 232 (6), 205 (8), 204 (52), 176 (12), 146 (12), 145 (100), 117 (34), 116 (7), 90 (6), 59 (7). $C_{13}H_{14}N_2O_4$ (262.3): calcd. C 59.54, H 5.38, N 10.68; found C 59.74, H 5.19, N 10.57.

Reaction of Cyclopentene with DMTD: This reaction was described previously,[10] but only **16** was isolated instead of its dihydro derivative because of autoxidation of the latter. We proceeded as in the case of norbornene (see above) and filtered the resulting reaction mixture (solvent: CH_2Cl_2) through basic aluminium oxide (activity III), which was then washed with methanol. The combined eluates were concentrated in vacuo. By dissolution of the residue in ethyl acetate and evaporation of the solvent in vacuo, a yellow powder, m.p. 109 °C, was obtained in 87% yield, which was shown to consist of dimethyl 4a,5,6,7-tetrahydro-2*H*-cyclopenta[*d*]pyridazine-1,4-dicarboxylate and **16** (see below) in a ratio of 7:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.67−1.79 (m, 2 H), 1.86 (m, 1 H), 2.65 (m, 1 H), 2.67−2.82 (m, 2 H), 3.11 (ddt, *J* = 10.5, 7.2, 2.8, 1 H, 4a-H), 3.83 (s, 3 H, CH_3), 3.84 (s, 3 H, CH_3), 8.18 (br s, 1 H, 2-H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 24.3, 29.4, and 31.6 (C-5,6,7), 39.4 (C-4a), 52.2 (2 CH_3), 122.4 (C-7a), 131.0 and 131.7 (C-1,4), 161.8 and 164.5 (2 C=O) ppm. IR (KBr): $\tilde{\nu}$ = 1715 cm^{-1} (C=O), 1698 (C=O). MS (70 eV, EI): *m*/*z* (%) = 238 (20) [M$^+$], 210 (45), 195 (49), 179 (100), 178 (17), 152 (26), 93 (31), 92 (19), 66 (22), 65 (21), 59 (18), 39 (17).

6,7-Dihydro-5*H*-cyclopenta[*d*]pyridazine (16): A solution of the product obtained in the preceding experiment (180 mg, 0.756 mmol) in dichloromethane (10 mL) was stirred at room temperature under oxygen overnight. The solvent was then evaporated in vacuo, and the residue was recrystallised from ethyl acetate to give pure **16** (96.0 mg, 54%) as pale yellow needles; m.p. 193−194 °C (ref.[10] 187 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 ("quint", line distance 7.8 Hz, 2 H, 6-H), 3.35 ("t", line distance 7.8 Hz, 4 H, 5,7-H), 4.03 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): Scheme 4. IR (KBr): $\tilde{\nu}$ = 1725 cm^{-1} (C=O). MS (70 eV, EI): *m*/*z* (%) = 236 (4) [M$^+$], 206 (5), 179 (5), 178 (38), 120 (10), 119 (100), 92 (5), 91 (6), 65 (6), 59 (6), 40 (18), 39 (6).

X-ray Crystal Structure Determination of Compounds 13−16: The data were collected from shock-cooled crystals with a BRUKER SMART-APEX diffractometer (graphite-monochromated Mo-K_α radiation, λ = 71.073 pm) equipped with a low-temperature device at 193(2) K.[30] The structures were solved by direct methods (SHELXS-NT 97)[31] and refined by full-matrix least-squares methods against F^2 (SHELXL-NT 97).[32] *R* values defined as $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$, $P = 1/3[\max(F_o^2,0) + 2F_c^2]$ (Table 1). SADABS 2.0 was employed as a program for empirical absorption correction.[33] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms 5-H and 7-H in **13** and 5-H, 6-H, 7-H and

Table 1. Crystal data and structure refinements for **13**−**16**

	13	**14**	**15**	**16**
Empirical formula	$C_{12}H_{12}N_2O_4$	$C_{12}H_{10}N_2O_4$	$C_{13}H_{14}N_2O_4$	$C_{11}H_{12}N_2O_4$
Formula mass	248.24	246.22	262.26	236.23
Colour	pale yellow	pale yellow	pale yellow	pale yellow
Dimensions [mm]	0.4 × 0.3 × 0.2	0.3 × 0.2 × 0.1	0.3 × 0.3 × 0.15	0.3 × 0.3 × 0.3
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group, *Z*	*Pnma*, 4	$P2_1/c$, 4	$P2_1/c$, 4	$C2/c$, 4
a [pm]	2148.32(3)	1141.04(5)	698.27(9)	1360.85(9)
b [pm]	684.370(10)	1310.86(5)	827.21(11)	1247.91(8)
c [pm]	780.360(10)	757.50(3)	2099.60(27)	687.91(5)
β [°]	90	106.848(3)	93.631(2)	110.4820(10)
V [nm^3]	1.14732(3)	1.08439 (8)	1.2103(3)	1.09437(13)
T [K]	193(2)	193(2)	193(2)	193(2)
$\rho_{calcd.}$ [Mg·m^{-3}]	1.437	1.508	1.439	1.434
Reflections collected	10170	9620	12807	3195
Unique reflections	1072	1872	2099	1309
$2\Theta_{max}$ [°]	24.76	24.84	24.84	28.77
No. of parameters	115	181	202	83
*R*1, *wR*2 for [$I > 2\sigma(I)$]	0.0447, 0.1159	0.0849, 0.1743	0.0690, 0.1752	0.0444, 0.1253
Residual electron density [10^{-6} e pm^{-3}]	0.174	0.292	0.417	0.234
Goodness of fit	1.125	1.313	1.099	1.063
CCDC no.	186742	186743	186744	186745

8-H in **14** were located by difference Fourier syntheses and refined freely. All other hydrogen atoms of the molecules were refined using a riding model. Supplementary crystallographic data for the structures **13**−**16** (CCDC-186742−186745) can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] [1a] N. L. Frank, K. K. Baldridge, J. S. Siegel, *J. Am. Chem. Soc.* **1995**, *117*, 2102−2103. [1b] A different synthesis gave a much better yield: A. Matsuura, K. Komatsu, *J. Am. Chem. Soc.* **2001**, *123*, 1768−1769.
[2] H.-B. Bürgi, K. K. Baldridge, K. Hardcastle, N. L. Frank, P. Gantzel, J. S. Siegel, J. Ziller, *Angew. Chem.* **1995**, *107*, 1575−1577; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1454.
[3] N. L. Frank, K. K. Baldridge, P. Gantzel, J. S. Siegel, *Tetrahedron Lett.* **1995**, *36*, 4389−4392.
[4] R. Rathore, S. V. Lindeman, A. S. Kumar, J. K. Kochi, *J. Am. Chem. Soc.* **1998**, *120*, 6012−6018.
[5] S. Cossu, O. De Lucchi, V. Lucchini, G. Valle, M. Balci, A. Dastan, B. Demirci, *Tetrahedron Lett.* **1997**, *38*, 5319−5322, and references therein.
[6] W. L. Jorgensen, W. T. Borden, *J. Am. Chem. Soc.* **1973**, *95*, 6649−6654.
[7] W. L. Jorgensen, W. T. Borden, *Tetrahedron Lett.* **1975**, 223−226.
[8] R. Gleiter, P. Bischof, K. Gubernator, M. Christl, L. Schwager, P. Vogel, *J. Org. Chem.* **1985**, *50*, 5064−5069.
[9] M. Christl, S. Freund, *Chem. Ber.* **1985**, *118*, 979−999.
[10] M. Avram, I. G. Dinulescu, E. Marica, C. D. Nenitzescu, *Chem. Ber.* **1962**, *95*, 2248−2253.
[11] [11a] J. Sauer, G. Heinrichs, *Tetrahedron Lett.* **1966**, 4979−4984. [11b] W. Dittmar, G. Heinrichs, A. Steigel, T. Troll, J. Sauer, *Tetrahedron Lett.* **1970**, 1623−1627.
[12] K. Peters, E.-M. Peters, C. Cohrs, H. Reuchlein, M. Christl, *Z. Kristallogr. NCS* **2000**, *215*, 601−602.
[13] K. Peters, E.-M. Peters, C. Cohrs, M. Christl, *Z. Kristallogr. NCS* **2000**, *215*, 53−54.
[14] S. Shaik, A. Shurki, D. Danovich, P. C. Hiberty, *Chem. Rev.* **2001**, *101*, 1501−1539.
[15] A. Stanger, *J. Am. Chem. Soc.* **1991**, *113*, 8277−8280.
[16] R. Gleiter, K. Gubernator, M. Eckert-Maksić, J. Spanget-Larsen, B. Bianco, G. Gandillon, U. Burger, *Helv. Chim. Acta* **1981**, *64*, 1312−1321.
[17] J. Spanget-Larsen, K. Gubernator, R. Gleiter, E. W. Thulstrup, B. Bianco, G. Gandillon, U. Burger, *Helv. Chim. Acta* **1983**, *66*, 676−686.
[18] [18a] R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, **1989**. [18b] R. M. Dreizler, E. K. U. Gross, *Density Functional Theory*, Springer, Berlin, **1990**. [18c] K. Burke, *Density Functional Theory and The Meaning of Life*, Department of Chemistry, Rutgers University, 610 Taylor Rd, Piscataway, NJ 08854, **2000**.
[19] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648−5652.
[20] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785−789.
[21] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257−2261.
[22] [22a] J. B. Foresman, A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, Gaussian Inc., Pittsburgh, PA 15213, USA, **1993**. [22b] J. W. Ochterski, *Thermochemistry in Gaussian*, http://www.gaussian.com, **2000**.
[23] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98* (Revision A.7), Gaussian, Inc., Pittsburgh, PA, **1998**.
[24] J. Gauss in *The Encyclopedia of Computational Chemistry* (Eds.: P. v. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. Kollman, H. F. Schaefer, III, P. R. Schreiner), Wiley, Chichester, **1998**, pp. 485−497.
[25] G. D. Purvis, R. J. Bartlett, *J. Chem. Phys.* **1982**, *76*, 1910−1918.
[26] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479−483.
[27] T. H. Dunning, Jr., *J. Chem. Phys.* **1989**, *90*, 1007−1023.
[28] *MOLPRO*, a package of ab initio programs designed by H.-J. Werner and P. J. Knowles, version 2002.1, R. D. Amos, A. Bernhardsson, A. Berning, P. Celani, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, P. J. Knowles, T. Korona, R. Lindh, A. W. Lloyd, S. J. McNicholas, F. R. Manby, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schütz, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, H.-J. Werner.
[29] [29a] C. Hampel, K. A. Peterson, H.-J. Werner, *Chem. Phys. Lett.* **1992**, *190*, 1−12. [29b] C. Hampel, K. A. Peterson, H.-J. Werner, *Chem. Phys. Lett.* **1992**, *192*, 332. [29c] M. J. O. Deegan, P. J. Knowles, *Chem. Phys. Lett.* **1994**, *227*, 321−326.
[30] [30a] D. Stalke, *Chem. Soc. Rev.* **1998**, *27*, 171−178. [30b] T. Kottke, R. J. Lagow, D. Stalke, *J. Appl. Crystallogr.* **1996**, *29*, 465−468. [30c] T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615−619.
[31] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.
[32] G. M. Sheldrick, *SHELXL-NT 97, Program for Crystal Structure Refinement*, Universität Göttingen, **1997**.
[33] G. M. Sheldrick, *Program for Empirical Absorption Correction*, Universität Göttingen, **2000**.

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