# Thermochemistry of Bridged-ring Substances. Enthalpies of Formation of Diamantan-1-, -3-, and -4-ol and of Diamantanone

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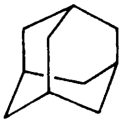
The enthalpies of combustion and of sublimation of four mono-oxygenated diamantanes have been determined. The derived solid and gas-phase enthalpies of formation in kcal $mol^{-1}$ at 298.15 K follow: diamantanone, −81.16 ±0.38, −56.53 ± 0.41; diamantan-1-ol, −102.49 ± 0.24, −74.30 ± 0.28; diamantan-3-ol, −98.89 ± 0.35, −71.14 ± 1.10; diamantan-4-ol, −103.96 ± 0.39, −75.80 ± 0.39. Oxo and hydroxy group increments within the diamantane, adamantane, and cyclohexane series are discussed. Enthalpy differences between the isomeric diamantanols are compared with existing data from equilibration studies in solution. Comparisons are made between the experimental gas-phase enthalpies of formation and those obtained by molecular mechanics (empirical force field) calculations based on the Allinger MM1 force field model.

THE enthalpies of formation and strain energies of polycyclic organic molecules are of considerable importance and have aroused much discussion.[1,2] In particular, the application of empirical methods to the determination of both energies and structures of quite large molecules has become quite extensive in recent years. At present, the most widely applicable empirical method is based on molecular mechanics (or force field) calculations.[3] Polycyclic hydrocarbons provide an important testing ground for empirical calculations, and in recent publications [4] we have demonstrated how calorimetric combustion studies with the diamondoid hydrocarbons adamantane (1), diamantane (2), and their methyl derivatives, can be used to probe deficiencies in the older force field models [5] and highlight improvements with the more recent Allinger MM2 force field.[6] With the advent of MM2 the performance of the molecular mechanics approach to the enthalpies and structures of a wide range of saturated hydrocarbons can now be considered comparable in accuracy with experimental methods.[4a] However, the general lack of experimental data for accurate parameterisation of the various force field models renders the situation with organic molecules containing the common functional groups much less satisfactory.[7]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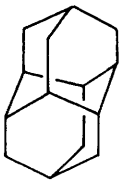
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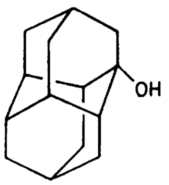
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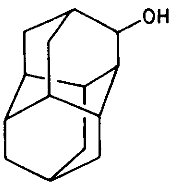
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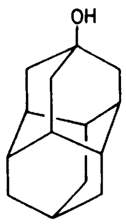
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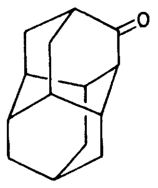
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In extending our evaluation of structure–energy relationships to include molecules containing functional groups we have measured the enthalpies of combustion and of sublimation of the isomeric diamantan-1-, -3-, and -4-ols (3)—(5) and of diamantanone (6). The thermochemistry of these systems is of interest because they provide much needed data on the effect of heteroatomic substitution on the enthalpies and strain energies of highly rigid polycyclic systems related to cyclohexanol and cyclohexanone. Furthermore, the combustion data for the three alcohols complement the limited amount of information available from isomerisation enthalpies obtained by the equilibration studies reported earlier.[8]

## RESULTS AND DISCUSSION

A summary of typical combustion experiments and of the combustion results is available as Supplementary Publication No. SUP 22851 (3 pp.).‡ The Table§ lists the results derived from the experimental data at 298.15 K with uncertainties twice the standard deviation from the mean calculated as recommended by Rossini and Deming.[9] The values of $\Delta E_c°$ and $\Delta H_c°$ are for the idealised reactions:

$$\text{diamantanols } C_{14}H_{20}O(c) + 18\tfrac{1}{2}O_2(g) \longrightarrow 14CO_2(g) + 10H_2O(l)$$

$$\text{diamantanone } C_{14}H_{18}O(c) + 18O_2(g) \longrightarrow 14CO_2(g) + 9H_2O(l)$$

Since all four substances are solids at 298 K the standard enthalpy of formation, $\Delta H_f°(c)$, include the intermolecular binding energies of the condensed state, and since we wished to compare our data with those from molecular mechanics calculations, which refer to the ideal gas state at 298.15 K, it was necessary to measure the enthalpies of sublimation, $\Delta H_{sub.}$. This was done using the temperature scanning technique described

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‡ For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1979, Index issue.

§ Throughout the paper $kcal_{th}$ = 4.184 kJ.

previously.[10] The derived gas-phase enthalpies of formation, $\Delta H_f°(g)$, for all four compounds are collected in the Table; included also are the molecular mechanics predictions of the $\Delta H_f°(g)$ values. The measured $\Delta H_{sub.}$ values refer to temperatures slightly above 298 K. The corrections to 298 K are, however, not significant within the experimental error and so the experimental values have not been corrected. The MM1 values are those produced by the Allinger force fields for alcohols [11] and ketones.[12] As we have shown in our earlier paper,[4a] the MM1 force field for saturated hydrocarbons overestimates the thermochemical stability of adamantane and diamantane and their methyl derivatives. This deficiency is corrected by the MM2 force field which gives predictions for these molecules in close accord with experimental values. As the MM2 heats of formation for diamantanone and the diamantanols are not available we have corrected the MM1 values for all four compounds [ΔMM1 (corr.)] by allowing for the discrepancy between the measured value of the heat of formation of diamantane and the MM1 prediction. The MM1 and MM1 (corr.) predictions are summarised in the Table.

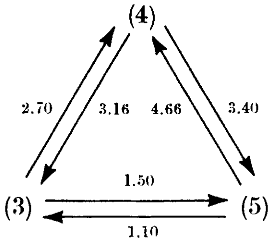
Comparison of the various sets of gas-phase data reveals a substantial difference between the experimental values and those predicted by MM1. When, however, the MM1 values are corrected as indicated in MM1(corr.) the accord between measurement and calculation is much improved. The experimental value is less exothermic for the three alcohols. In view of the low level of accuracy of MM1 predictions for hydrocarbons and the anticipated lower accuracy of predictions for alcohols and ketones this agreement is considered satisfactory. However, the fact that there is a systematic deviation of 1—2 kcal mol$^{-1}$ for all four compounds is less satisfactory, suggesting either a constant error in the force field or a systematic experimental error. Although the latter cannot be ruled out, it seems unlikely in view of the fact that our earlier work on related hydrocarbons yield heats of formation consistent with data from equilibration studies and in excellent accord with the MM2 force field predictions. We note also that the MM1 force field is in error by a similar magnitude and direction for the heat of formation of cyclohexanone,[12] although it accurately reproduces the heat of formation of cyclohexane. This suggests that the MM1(corr.) energies may contain a systematic force field error.

Derived thermochemical data at 298.15 K (kcal mol$^{-1}$)

| | Diamantan-1-ol (3) | Diamantan-3-ol (4) | Diamantan-4-ol (5) | Diamantanone (6) |
|---|---|---|---|---|
| | | Experimental | | |
| $-\Delta E_c°$ (c) | 1 894.71 ± 0.24 | 1 898.31 ± 0.35 | 1 893.24 ± 0.39 | 1 848.02 ± 0.38 |
| $-\Delta H_c°$ (c) | 1 897.38 ± 0.24 | 1 900.97 ± 0.35 | 1 895.91 ± 0.39 | 1 850.39 ± 0.38 |
| $-\Delta H_f°$ (c) | 102.49 ± 0.24 | 98.89 ± 0.35 | 103.96 ± 0.39 | 81.16 ± 0.38 |
| $\Delta H_{sub.}$ | 28.19 ± 0.14 | 27.75 ± 1.04 | 28.16 ± 0.05 | 24.63 ± 0.15 |
| (at $T$/K) | (334) | (338) | (337) | (320) |
| $-\Delta H_f°$ (g) | 74.30 ± 0.28 | 71.14 ± 1.10 | 75.80 ± 0.39 | 56.53 ± 0.41 |
| | | Molecular mechanics predictions | | |
| −MM1 | 79.29 | 76.62 | 79.87 | 61.53 |
| ΔMM1 | 4.99 | 5.48 | 4.07 | 5.00 |
| −MM1(corr.) | 75.70 | 73.03 | 76.28 | 57.94 |
| ΔMM1(corr.) | 1.40 | 1.87 | 0.48 | 1.41 |

ΔMM1 and ΔMM1(corr.) refer to the difference between measured and predicted values.

A further check on the reliability of the experimental data can be obtained by comparison of the relative thermochemical stabilities of the three diamantanols as measured by direct equilibration [8] with those expressed as heats of formation differences. The isomeric diamantanols are multiply-bridged cyclohexanols with topological differences arising from the three different ways in which the hydroxy-group can be attached to the diamantane nucleus. As we have shown earlier,[8] the three alcohols can be brought to thermodynamic equilibrium in concentrated sulphuric acid and measurement of the temperature dependence of the equilibrium constants for all three isomers produces the isomerisation enthalpies, $\Delta H_i°$, for each isomer pair. The results below show that there is very good agreement between the $\Delta H_i°$ data and the heats of formation differences, $\Delta\Delta H_f°(g)$:

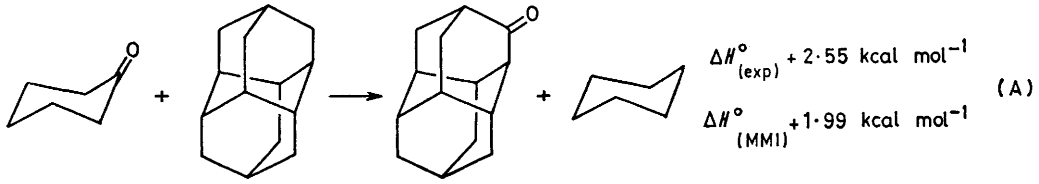


values outside = $\Delta H_i°$
values inside = $\Delta\Delta H_f°$ (g)
data in kcal mol$^{-1}$

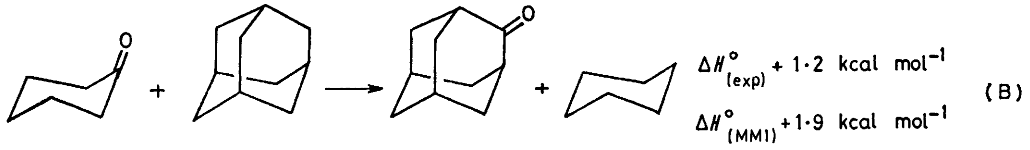
However, the agreement does not rule out a systematic error in the heats of formation of the alcohols.

The absolute magnitude of the experimental heats of formation can be checked using a chemical equation whose enthalpy change can be reliably checked by molecular mechanics, *i.e.* an equation in which all or most of the errors cancel each other out and which relies on external data. Such an equation was used earlier to demonstrate that the experimental enthalpies of formation of adamantane and diamantane are mutually consistent.[4a] Consider the hypothetical carbonyl exchange reaction shown for cyclohexanone + diamantane ⟶ cyclohexane + diamantanone [reaction (A)] and the analogous process of cyclohexanone + adamantane ⟶ cyclohexane + adamantanone [reaction (B)].

The enthalpies of formation of cyclohexane,[7] cyclohexanone,[7] adamantane,[4a] and diamantane [4a] are reliably established experimentally and the enthalpy of formation of adamantanone has recently been determined by Arora and Steele.[13] Using these literature values and our measured value for the enthalpy of formation of diamantanone we find that the enthalpy change of reaction (A) is 2.55 kcal mol$^{-1}$ endothermic and that of reaction (B) 1.2 kcal mol$^{-1}$ endothermic. Within the error limits these two enthalpy changes agree with the MM1 calculations and we can conclude that the experimental enthalpies of formation of the two diamondoid ketones are probably accurate to $\pm 1$ kcal mol$^{-1}$. Equations of types (A) and (B) represent a convenient way of expressing strain energy differences between pairs of related systems, in this case cyclohexane and cyclohexanone *versus* diamantane and diamantanone, and adamantane and adamantanone. That both reactions (A) and (B) are endothermic indicates that incorporating an $sp^2$ carbon atom into cyclohexane is less expensive in terms of enthalpy than is a similar change in either adamantane or diamantane. This is consistent with the nature of the monocyclic and polycyclic systems. The flexible nature of cyclohexanone enables it to relax into a flattened geometry in which the various components of strain energy are minimised. The inflexible nature of the diamondoid skeleton, on the other hand, renders the introduction of an $sp^2$ carbon atom into an environment in which all the bond angles are near to the tetrahedral value for $sp^3$ carbon atoms much less favourable. An *X*-ray diffraction study [14] of an adamantanone derivative reveals the extent of distortion at several carbon atoms caused by the widened angle at the carbonyl carbon atom.

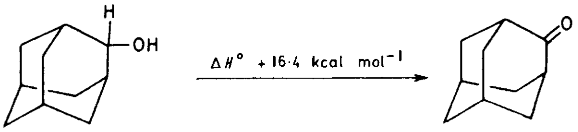


(A)

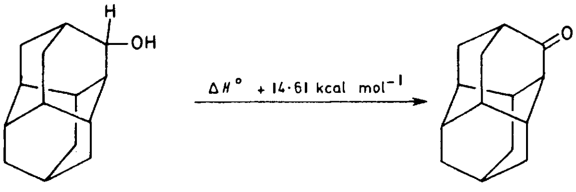


(B)

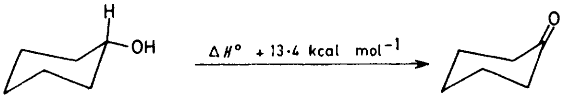
The equilibration studies with the isomeric diamantanols suggest that they are reliably calibrated relative to each other but do not provide any information on external consistency. Arora and Steele [13] have provided the enthalpy change for the oxidation of adamantan-2-ol to adamantanone (C) and we can now compare their value of +16.4 kcal mol$^{-1}$ with that of +14.61 kcal mol$^{-1}$ obtained in the present work for the comparable change of diamantan-3-ol into diamantanone (D). The enthalpy change for the oxidation of cyclohexanol to cyclohexanone [reaction (E)] is +13.4 kcal mol$^{-1}$.[7] Once again agreement between the independently determined sets of numbers for the two diamondoid systems (C) and (D) is very satisfactory, considering the fact that the 2 kcal mol$^{-1}$ extra strain energy of adamantanone and diamantanone leads to a prediction of +15.4 kcal mol$^{-1}$ for the enthalpy change for both oxidation reactions. This prediction is based on the reasonable assumption that the hydroxy-group has approximately the same effect on the strain energy of all three alcohols. As expected, oxidation of adamantan-2-ol and diamantan-3-



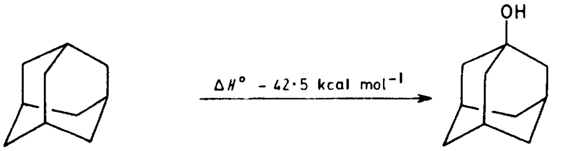
(C)



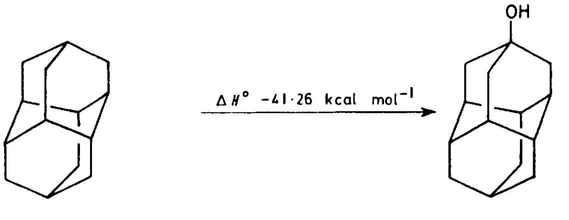
(D)



(E)



(F)



(G)

ol is more endothermic than is oxidation of cyclohexanol due to the greater distortion associated with the $sp^2$ carbon atom in the rigid systems.

A final external check which can be applied to our data concerns the group increment for replacing a bridgehead hydrogen atom in adamantane and diamantane by a hydroxy-group. The work of Arora and Steele [13] gives a value of $-73.4$ kcal mol$^{-1}$ for the heat of formation of adamantan-1-ol which when combined with our value of $-31.76$ kcal mol$^{-1}$ for the heat of formation of adamantane gives a hydroxy-group bridgehead increment of $-42.5$ kcal mol$^{-1}$ (F). The corresponding bridgehead group increment (G) in the diamantane series is $-41.26$ kcal mol$^{-1}$, in agreement with the adamantane series. As the diamantan-4-ol heat of formation is satisfactorily linked to its two isomers (**3**) and (**4**) *via* the equilibration studies we can conclude that our data, together with those of Arora and Steele [13] for adamantanone and the two adamantanols and our earlier data for the corresponding hydrocarbons,[4a] form a consistent, reliable set, probable errors being of the order of $\pm 1$ kcal mol$^{-1}$, in accord with the experimental uncertainties.

## EXPERIMENTAL

Diamantanone (**6**) was prepared by oxidation of diamantane in 96% sulphuric acid using a procedure described previously.[15] It was also prepared by chromic acid oxidation of diamantan-3-ol. Purification of both samples was by column chromatography initially. Further purification was by vacuum sublimation followed by zone-melting (24 molten zone passes for each). Within experimental error the two samples of diamantanone had the same heat of combustion. Diamantan-1- and -4-ol (**3**) and (**5**) were obtained as a 1 : 1 mixture by hydrolysis of the corresponding chloride mixture using a published procedure,[15] and were separated by column chromatography over alumina. Diamantan-3-ol (**4**) was prepared by lithium aluminium hydride reduction of diamantanone and was purified as described for the other isomers. G.l.c. and d.s.c. analysis indicated that there were no impurities in any of the four compounds above 0.05%. M.p.s by d.s.c. (Perkin-Elmer d.s.c. 2, sealed pans) were diamantanone, 522—523 K; diamantan-1-ol, 573 K; diamantan-3-ol, 484 K; and diamantanone, 530 K. The calorimeter used was the Belfast Mark 1 aneroid system described previously.[4a] The operating details were exactly as described as was the technique of sample encapsulation. However, because of their ease of combustion the diamantanols were burnt at 20 atm. oxygen pressure, rather than the 40 atm. used with diamantanone and in the previous work. Heats of sublimation were measured by the temperature scanning technique described previously.[10]

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