

Barriers to Internal Rotation in 1,3,5-Trineopentylbenzenes. IX. Force Field Calculations and ^{13}C and ^2H NMR Relaxation Measurements on 1,3,5-Trineopentylbenzene

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The barrier to internal rotation of a neopentyl group in 1,3,5-trineopentylbenzene (TNB) has been experimentally estimated by means of ^{13}C and ^2H NMR relaxation time measurements. The resulting upper-limit barrier values (~ 20 and 22 kJ mol^{-1}) are compatible with previously obtained estimates from low-temperature NMR bandshape analysis on a model compound (23 kJ/mol), and from empirical force field molecular mechanics calculations (24 kJ/mol). More detailed force field calculations on TNB and the internal rotational barrier have now been performed with Allinger's MM1 program. In the initial state, attractive steric interactions among the neopentyl groups are again found to lower the energy of the rotamer with all three neopentyls on the same side of the ring plane by *ca.* 4 kJ/mol compared with the rotamer where one neopentyl group has rotated 180° . The barrier height calculated with MM1 is 31 kJ/mol .

Molecular mechanics calculations with the BIGSTRN program package^{1,2} on 1,3,5-trineopentylbenzenes (TNB's), using Allinger's 1971 force field,³ provided support for an interpretation of experimental results^{4,5} (^1H , ^{13}C NMR) on 2,4,6- Br_3TNB , $-\text{Cl}_3\text{TNB}$ and $-\text{CH}_3)_3\text{TNB}$ in terms of attractive steric effects among *tert*-butyl groups on the same side of the ring plane.⁶ When Allinger's MM1 program (1973 force field^{7–11}) became available to us,* we decided to take advantage of its very efficient minimization routine and its dihedral angle "driver"^{7–9} to undertake a more thorough exploration of the internal

rotational energy barrier than was economically feasible with BIGSTRN.

The results of our calculations are reported in this paper, along with an experimental estimate of the barrier in TNB itself. We have attempted to use ^{13}C and ^2H relaxation times for this purpose, and we were able to obtain an upper-limit value for the barrier, which is in satisfactory agreement with a previous (indirect) experimental estimate based on NMR line-shape measurement on a model compound,¹² and with the molecular mechanics calculations.

RESULTS

^{13}C NMR relaxation times. Carbon-13 NMR spin-lattice relaxation times (T_1) were measured for both the unsubstituted aromatic carbons and the benzylic carbons in TNB. Nuclear Overhauser effect (NOE) measurements showed that the relaxation of the benzylic and aromatic carbons is completely dominated by dipolar relaxation.

In order to use the relaxation times to calculate the correlation time for the overall motion of the molecule and that for the internal rotation of the neopentyl groups, the following assumptions were made:¹³ (1) the molecule as a whole tumbles isotropically (*i.e.* it may be approximated as a sphere); (2) the internal rotation can be described as a diffusion process, *i.e.* it can be thought to proceed *via* a large number of small steps.

With these assumptions, the equation due to Woessner^{14,15} can be used to calculate the correlation time for the internal rotation. We have used

* The MM1 program was kindly placed at our disposal by Dr. T. Liljefors, University of Lund.

the Woessner equation in the form given by Brevard, Kintzinger and Lehn:¹⁶

$$T_1^{-1} = AT_{1m}^{-1} + kB(\tau_m^{-1} + \tau_i^{-1})^{-1} + kC[\tau_m^{-1} + 4(\tau_i)^{-1}]^{-1} \quad (1)$$

Here T_1 is twice the observed T_1 value for the benzylic carbons (twice because they are each bound to two protons), and T_{1m} is the dipolar contribution to the relaxation of the unsubstituted aromatic carbons. $\tau_m (= kT_{1m})^{-1}$ and τ_i are the correlation times for the overall molecular motion and the internal motion, respectively, and A , B , C and k are defined as follows:

$$A = \frac{1}{4}(3 \cos^2 \theta - 1)^2, \quad B = \frac{3}{4} \sin^2 2\theta, \quad C = \frac{3}{4} \sin^4 \theta$$

$$k = \mu_0^2 (4\pi)^{-2} \cdot \gamma_H^2 \gamma_C^2 \hbar^2 r_{C-H}^{-6},$$

$$\mu_0 (4\pi) = 10^{-7} (\text{NA}^{-2})$$

γ_H and γ_C are the gyromagnetic ratios for the proton and carbon-13 nuclei r_{C-H} is the carbon-proton bond distance and θ is the angle between the internal rotation axis and the C-H bond vector. The angle θ (110.1°) and the carbon-proton distances r_{C-H} (1.0910 and 1.0968 Å for the aromatic and benzylic bonds, respectively) were obtained from our molecular mechanics calculations. However, Stark *et al.*¹⁷ have shown that the r_{C-H} value to be used for the bond length of the aromatic hydrogens should be 1.114 Å instead of the "normal" 1.09 Å* (which gives $k = 18.3 \times 10^9 \text{ s}^{-2}$). Since no "corrected" value for the bond length of the benzylic protons was given by Stark *et al.*, we used a value of 1.1198 Å, which is the value

* Because effects of vibrational averaging must be taken into account.^{18,19}

for the aromatic hydrogen bond plus the bond length difference found from our molecular mechanics calculations.

The free energy of activation (ΔG^\ddagger) was calculated *via* the Eyring equation²⁰ from the correlation time for the internal rotation (τ_i). The results are collected in Table 1.

²H NMR relaxation times. The deuterium spin-lattice relaxation times for aromatic and benzylic deuterons were measured on a solution containing equal amounts of two compounds specifically deuterated in the ring or in the benzylic position. From these relaxation times, the correlation time for the internal rotation can be calculated in a way completely analogous to that used for the ¹³C data. In this case, the constant in eqn. (1) becomes k_q , given by

$$k_q = \frac{3}{8} \left(\frac{e^2 q Q}{\hbar} \right)^2$$

where e is the electronic charge and q is the electric field gradient at the nucleus of quadrupole moment Q .

Assuming that the deuterium quadrupole coupling constant ($e^2 q Q / \hbar$) for both sp^3 - and sp^2 -type C-D bonds is 170 kHz^{16,21}, the value of k_q appropriate for the benzylic and the aromatic deuterons is $0.43 \times 10^{12} \text{ s}^{-2}$. The calculated τ_i interval and the resulting free energies of activation are given in Table 1.

Another use of the measured ¹³C and ²H relaxation times could be to estimate values for the quadrupole coupling constants.²² Jackman *et al.*²² used this approach for phenyl (²H₁) acetylene and (²H₆) benzene and calculated the quadrupole coupling constants from eqn. (2).

Table 1. ¹³C and ²H relaxation times^a, correlation times^a and calculated free energies of activation.

Nucleus	T/°C	T ₁ /s	T _{1m} /s	τ/10 ⁻¹² s	τ _m /10 ⁻¹² s	τ _i /10 ⁻¹² s	ΔG [‡] /kJmol ⁻¹	Solvent	Spectrometer
¹³ C	28	2.28(0.11) ^{b,c}	1.73(0.08) ^{b,c}	24(1)	31(1)	200–380	19(1)	CD ₃ COCD ₃	JEOL FX-60
¹³ C	28	1.80(0.10) ^{b,d}	1.36(0.10) ^{b,d}	31(1)	39(2)	230–570	19(1)	CDCl ₃	JEOL FX-60
¹³ C	27	1.82(0.08) ^{b,e}	1.45(0.07) ^{b,e}	30(1)	37(2)	290–710	20(1)	CDCl ₃	Varian XL-10
² H	27	0.0579(0.0018) ^{b,e}	0.0514(0.0010) ^{b,e}	40(1)	46(1)	630–1530	22(1)	CHCl ₃	Varian XL-10

^a T_1 , T_{1m} refers to measured T_1 values for benzylic carbons (deuterons) and aromatic unsubstituted carbons (deuterons). τ , τ_m and τ_i are the correlation times for benzylic carbons (deuterons), correlation time for molecular motion and correlation time for internal rotation. ^b All errors are 3 σ . In the case of ²H the τ and τ_m values are calculated by using the quadrupole coupling constant equal to 170 kHz (see text). All T_1 values from ¹³C relaxation times are twice the measured relaxation times (due to two protons). ^c Mean value of three measurements. ^d Two measurements. ^e Single measurement.

$$(e^2 Qq/h) = 49.3 r_{C-H}^{-3} (T_1^{DD}/T_1^Q)^{1/2} \text{ (kHz)} \quad (2)$$

where T_1^{DD} and T_1^Q are the measured ^{13}C and ^2H spin-lattice relaxation times, and r_{C-H} is the carbon-hydrogen bond length in Ångströms.

Using the mean values of the ^{13}C and ^2H relaxation times for TNB in CDCl_3 solution (see Table 1), we obtain benzylic and aromatic C–D quadrupole coupling constants equal to 196 ± 7 and 186 ± 7 kHz, respectively.

Force field calculations. Allinger's molecular mechanics program MM1 (1973 force field)^{7–11} was used to calculate conformational energies along the potential surface for the rotation of one of the neopentyl groups in the lowest energy rotamer of TNB, with rotation angle increments of 5° . (See Fig. 1, curve A. The driving angle $\theta_{1,278}$ is defined in Fig. 2).

In the calculations, all of the bond lengths and bond angles, as well as the torsional angles, except for that describing the rotation of the neopentyl group, were allowed to relax. For some selected

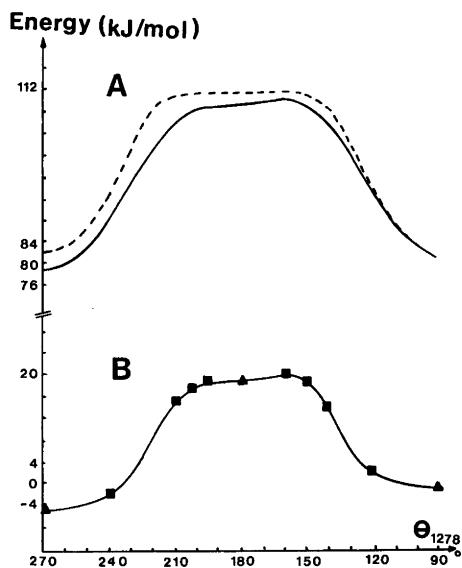


Fig. 1. Potential curves for the internal rotation of a neopentyl group in TNB by using the force field program MM1 (curve A) and the BIGSTRN program (curve B) as a function of the driving angle $\theta_{1,278}$. Values marked \blacktriangle are taken from Ref. 6.

The dashed curve shows the energy profile for one of the isomers "A, B and C"⁶ by rotating one of the two neopentyls on the same side of the ring plane (see text).

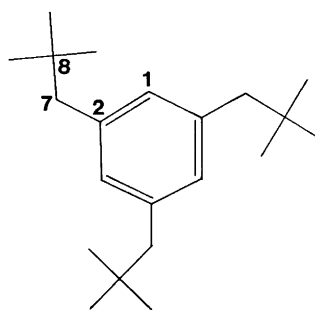


Fig. 2. Definition of the driving angle $\theta_{1,278}$ used in TNB.

torsional angles, the conformation obtained from the MM1 program was used as the starting conformation for calculations with the BIGSTRN^{1,2} program,* which uses Allinger's 1971 force field.³ The energies resulting from these calculations are also shown in Fig. 1 (curve B).

The various energy contributions to the total strain energy for the two low-energy conformations and for the transition state are collected in Table 2.

DISCUSSION

Molecular mechanics calculations. Our previous calculations on TNB⁶ were carried out with the BIGSTRN^{1,2} program package on a limited number of rotamers, *viz.* that with all three *tert*-butyl groups on the same side of the ring plane ("rotamer D"⁶) that with two on one side and one on the other (three identical ones, "rotamers A,B,C"⁶), and a rotamer with one neopentyl group twisted 90° from the starting conformation in "D". The energy profiles calculated with the BIGSTRN and MM1 programs are compared in Fig. 1. In the critical transition state region, the shapes of the energy profiles are quite similar, even though the *total* energies differ by 80–90 kJ/mol (Fig. 1). The difference in the total energies results from differences in the force fields used,^{1,2,7–11} as well as from the inclusion of an energy term resulting from a π -electron system calculation in the MM1 program.⁷ Both force fields indicate the operation of attractive steric interactions to be the dominant source of the energy difference between the two low-energy conformations (*cf.* Table 2).

* Kindly placed at our disposal by Professor Kurt Mislow, Princeton University.

Table 2. Calculated rotational barriers. Different energy contributions and total conformational energy (kJ/mol).

	Rotamer				Rotamer		
	270	θ_{1278}^a 162	90		270 ^c	θ_{1278}^b 162	90 ^c
Compress	13.06	14.82	13.15	Bond-stretch	12.60	14.95	12.56
Bending	23.11	32.28	22.69	Angle-stretch	24.37	34.46	24.16
Stretch-bend	1.93	2.51	1.88	Torsion-stretch	0.84	3.73	0.75
Van der Waals (1.4)	46.85	49.70	46.73	Nonbond-stretch	-39.27	-28.72	-35.17
Van der Waals (other)	-27.51	-17.59	-23.70	Out of plane stretch	0.13	0.08	0.08
Torsion	20.89	28.26	20.81	Stretch-bend	-3.02	-4.48	-3.02
Torsion-bend	-0.00	-0.92	-0.00	Total	-4.35	20.01	-0.64
Dipole	0.54	0.54	0.50				
Total	78.87	109.6	82.06				

^a Calculated by the Allinger force field program MM1 on the TNB system. ^b Calculated by the STRAIN program on the TNB system. ^c These calculations are taken from Ref. 6.

The asymmetry in the transition states in curves A and B shows the effect of attractive steric interactions. When one neopentyl group rotates so as to increase the distance between its *t*-butyl group and the other two *t*-butyl groups, the steric attraction among the *t*-butyl groups should decrease. This decreased steric attraction is one of the contributions (see Table 2) to effect the total conformational energy (E_{strain}) to be at a maximum (transition state) when the rotating group has its *t*-butyl group *ca.* 20° above the ring plane and the other two *t*-butyl groups below the plane. This geometry is shown in a stereoplot in Fig. 3. From this plot, and also from the calculations, it is seen what has been pointed out by Carter and Stilbs,⁶ that the "reaction coordinate" is primarily a combination of twisting about the

$C_{Ar}-CH_2$ and CH_2-C- bonds.

A detailed inspection of the conformations at and close to the transition state given by the two programs shows that there are only minor differences. The largest difference is realized for the rotating neopentyl's methyl group closest to the ring, whose torsional angle (def. as the angle

$CH_3-C-CH_2-C_{Ar}$) differs by 2–4° between

the two programs in the nearness of and at transition state.

Calculations were also made starting with one of the three identical rotamers "A, B and C"⁶ and rotated one of the two neopentyls on the same side of the ring plane. We found the energy profile, shown as the dashed curve in Fig. 1A. From this energy profile (and from the calculations) we can see that the energy of activation in this case is *ca.* 30 kJ/mol, and the energy profile is not

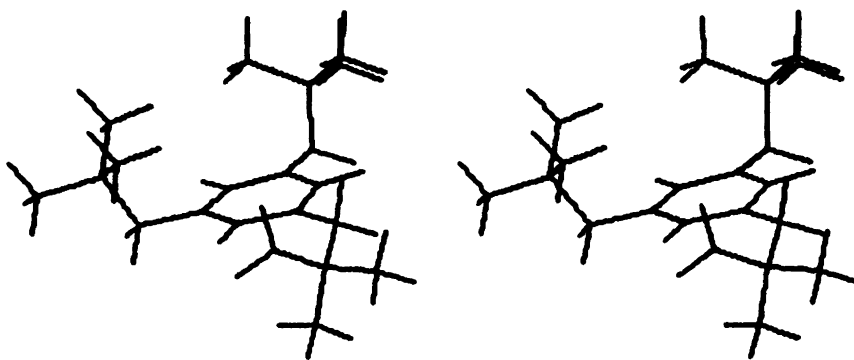


Fig. 3. Stereo plot of the transition state for internal rotation of a neopentyl group in TNB.

symmetric although it may look so at a first glance. As the two energy profiles in Fig. 1A show nearly the same amount of free energies of activations, (31 and 30 kJ/mol. resp.) this implies that internal rotation along the dashed curve in Fig. 1A is as possible as rotation along the other curve for each of the rotamers "A, B and C".

The rotational barrier calculated with MM1 (31 kJ/mol) is slightly higher²³ than that reported previously⁶ (24 kJ/mol; see Table 2). Both calculated barriers are in reasonable agreement with experimentally estimated upper limit of 23 kJ/mol, based on an attempted NMR band shape study of a model compound, 3,5-di-*tert*-butylneopentylbenzene. (The decoalescence of the $-\text{CH}_2$ -signal at low temperature could not be observed, only a broadening attributed to exchange.)¹² Since there are at least two routes by which a conformational change from one rotamer to another can take place and in NMR bandshape studies only the total process is observed, the observed value has to be corrected to take this into account before comparing with calculated barriers. However, if there are only two routes with the same activation energy the correction is only $RT \ln 2$ (1.7 kJ/mol at 300 K) on the free energy of activation.

¹³C and ²H relaxation times. A literature survey²⁴ shows that there is an appreciable spread in the quadrupole coupling constants estimated by various methods. It is therefore difficult to know what value to use in this work, when we want to use the ²H relaxation times to estimate the correlation time for the internal rotation of the neopentyl groups. As shown in the results section, the ¹³C and ²H relaxation times can be used to calculate the ²H quadrupole coupling constant, resulting in values in good agreement with other quadrupole coupling constants obtained in the same way.²² However, we need an independent measure of the quadrupole coupling constants to be able to use our relaxation times to estimate the effective correlation times for the deuterium nuclei. This, however, does not exist, and we have to choose among various reasonable values.²⁴

As we shall see the choice of quadrupole coupling constants can be critical for the calculated internal correlation time (τ_i). Suppose that both quadrupole coupling constants are 180 kHz, we get by applying the values in Table 1 and eqn. (1), $\tau_i = 8.1 \times 10^{-10}$ s. If we allow an uncertainty of ± 10 kHz in the quadrupole coupling constants, and attempt to calculate the extreme limits for the

internal correlation time (τ_i), we find at one extreme (benzylic 170 kHz; aromatic 190 kHz), eqn. (1) is not satisfied, while at the other (benzylic 190 kHz; aromatic 170 kHz) a $\tau_i = 2.6 \times 10^{-10}$ s is obtained.

Fortunately, as seen from Table 1, the large intervals in the calculated τ_i -values (due to errors in the estimated T_1 and T_{1m} values and used quadrupole coupling constants) will have little effect on the estimated free energies of activation. Our values agree well with the previously discussed measurements.^{6,12}

We believe that the present work shows that the barriers to internal rotation calculated from ²H relaxation time measurements are less reliable than those obtained from ¹³C relaxation times, unless the quadrupole coupling constants for the studied molecular system are known from another independent measurement. Fortunately as stated above errors in the τ_i -value (²H relaxation times) will have only little effect on the calculated free energy of activation, however, they should not be used in attempts to estimate activation enthalpies and entropies since they will most probably be seriously in error.

EXPERIMENTAL

The ¹³C NMR measurements were made on a JEOL FX-60 and on a Varian XL-100 spectrometer working at 15 and 25 MHz, respectively, for ¹³C. The ²H NMR measurements were made at 15 MHz on the Varian XL-100 spectrometer. In all cases the fast-inversion-recovery pulse sequence was used for relaxation time measurements. For the FX-60 ¹³C experiments the 90° pulse length was 13 μ s and the time between the sequences was 6 s. For the XL-100 spectrometer the 90° pulse length and the time between the sequences were 50 μ s and 6 s, and 30 μ s and 1 s for ¹³C and ²H experiments, respectively. Samples for ¹³C NMR measurements were degassed.

The relaxation times were evaluated by fitting the peak intensities to an exponential function with three adjustable parameters. The error limits are 3σ , where σ is the marginal standard deviation as defined by Mayne *et al.*²⁵

Routine proton NMR on synthesized products were run on a JEOL JNM 60 MHz spectrometer, mass spectra on an LKB MS 9000 mass spectrometer operating with 70 eV electron energy and IR on a Perkin Elmer model 257 grating infrared spectrometer. Melting points were obtained on a Kofler hot stage apparatus and are uncorrected.

The elementary analyses were made by Analytjänst at the University of Lund.

The force field calculations were made on the UNIVAC 1108 at the University of Lund.

SYNTHESIS

All materials were of reagent grade and were used without purification unless otherwise stated.

1,3,5-Trineopentylbenzene and 1,3,5-tripivaloylbenzene were synthesised as described by Martinson²⁶ and 1,3,5-trineopentyl-2,4,6-trideuteriobenzene as described by Olsson²⁷ (purity 98 %).

1,3,5-Tris(1-hydroxy-2,2-dimethylpropyl)benzene

(1). 1,3,5-Tripivaloylbenzene (2.0 g) dissolved in 15 ml of ether was added during cooling to a suspension of lithium aluminium hydride (6.9 g) in 200 ml of dry ether. The mixture was then refluxed and small aliquots were withdrawn, hydrolysed and studied by TLC (alumina with cyclohexane as eluent). After 24 h, TLC showed a single product and the reaction mixture was hydrolysed in turn with 15 ml of ethyl acetate, 5 ml of 10 % solution of sodium hydroxide and 5 ml of water. The mixture was filtered and the filtrate evaporated to dryness leaving a white solid residue, which was recrystallised from ethanol-water (1:1) leaving 1.7 g, yield 65 %. The NMR spectrum was in accordance with that published by Martinson²⁶ on 1,3,5-tris(1-hydroxy-2,2-dimethylpropyl)benzene. M.p. 214–215 °C (Lit. = 215 °C).²⁶

1,3,5-Tris(1-bromo-2,2-dimethylpropyl)benzene (2). Compound (1) (0.73 g) was dissolved in 50 ml of dry benzene. Dry gaseous hydrogen bromide (9.4 g) was then added and the reaction mixture was stirred at room temperature. The reaction was followed by TLC (alumina with cyclohexane as eluent) and after 4 days only one product was detectable. The solvent was evaporated and the brown residue left was decolourised by chromatography on a column of alumina with cyclohexane as eluent. After collection and evaporation of the solvent, 1.11 g of a white crystalline residue remained. Yield 92 %. M.p. 164–165 °C. (Found: 48.3; H 6.13; Br 45.6. Calc. for C₂₁H₃₃Br₃: C 48.03; H 6.33; Br 45.6) ¹H NMR (CCl₄): δ 1.03 (27 H, s, C(CH₃)₃), 4.73 (3 H, s, CHBr), 7.19–7.28 (3 H, m, arom. H). IR (γ_{max} CCl₄): 3010 (w), 2970 (vs), 2940 (s), 2910 (m), 2880 (m), 1600 (w), 1480 (s), 1460 (m), 1400 (m), 1370 (m), 1200 (w), 1160 (m), 1080 (w), 980 (w), 870 (m), 700 (w) cm⁻¹.

MS [*m/e* (%): 525(2), 523(5), 521(5), 519(2), 509(2), 507(2), 468(5), 445(14), 443(33), 441(14), 390(7), 388(11), 386(7), 365(11), 363(11), 309(5), 307(7), 267(7), 267(33), 266(5), 256(90), 215(5), 192(33), 128(67), 64(100), 57(67).

1,3,5-Tris(1-deuterio-2,2-dimethylpropyl)benzene (3). Compound (2) (0.32 g) was dissolved in 10 ml of dry tetrahydrofuran and added dropwise to a suspension of lithium aluminium deuteride (1.0 g) in 40 ml of dry tetrahydrofuran, during cooling. The mixture was then refluxed for 24 h and then hydrolysed in turn with 5 ml of ethyl acetate, 5 ml of 10 % solution of sodium hydroxide and 5 ml of water and then filtered. The filtrate was evaporated, leaving an oily residue which was decolourised by chromatography on a column of alumina with hexane as eluent. Evaporation of the solvent left 0.16 g of a white crystalline residue, m.p. 77–78 °C; yield 99 %.

¹H NMR (CDCl₃): δ 0.91 (27 H, s, -C(CH₃)₃), 2.43 (3H, s, -CHD-), 6.68 (3H, s, arom. H).

IR (γ_{max} CCl₄): 3020 (w), 2960 (vs), 2870 (s), 1605 (m), 1470 (s), 1450 (m), 1380 (m), 1370 (s), 1235 (m), 1205 (w), 870 (w), 740 (w) cm⁻¹. MS [*m/e* (%): 292(2), 291(45), 290(26), 288(9), 251(19), 250(35), 249(66), 248(11), 236(21), 235(66), 234(21), 220(21), 205(60), 180(16), 179(93), 178(52), 177(71), 176(19), 123(100), 122(48), 121(35).

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