Supporting Information

Computational design of a notable nitrogen-rich energetic compound on the basis of Diels-Alder reaction

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All involved computational details and formulas:

All geometry optimizations and frequency calculations were performed with DFT method at M06-2X/6-31G(d) and B3PW91/6-31G(d,p) levels by using Gaussian 09 software[1]. Frequency calculations ensure that reactants and products have not any imaginary frequency and the TSs have only one imaginary frequency. The intrinsic reaction coordinate (IRC) analyses confirmed that the TSs truly associate to the minima of the reactants and the products.

The ρ was predicted by equation (1):[2]

$$\rho = \alpha_1(M/V_m) + \beta_1(v\sigma^2_{tot}) + \gamma_1 \quad (1)$$

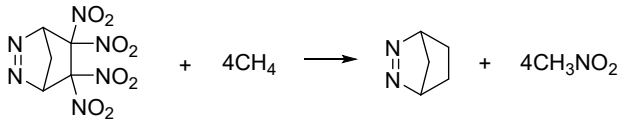
where M is the molecular weight (g.mol^{-1}); V_m is the average molar volume within the 0.001 a.u. electron density contour (cm^3.mol^{-1}); v is the degree of balance between positive and negative potential on the molecular surface; σ^2_{tot} is a measure of variability of the electrostatic potential (kcal^2.mol^{-2}); The coefficients α_1, β_1, and γ_1 at the B3PW91/6-31G(d,p) level are 0.9183, 0.0028, and 0.0443, respectively.[2]

The $\Delta H_f°$(s) was estimated using the following equations (2-3):[3]

$$\Delta H_f°(s) = \Delta H_f°(g) - \Delta H_{sub} \quad (2)$$

$$\Delta H_{sub} = \alpha_2 A_S^2 + \beta_2(v\sigma^2_{tot})^{0.5} + \gamma_2 \quad (3)$$

where $\Delta H_f°$(g) is the gas-phase heat of formation which was estimated by designing the following isodesmic reaction (4); ΔH_{sub} is the sublimation enthalpy; A_S is the area of the isosurface of 0.001 e/Bohr^3 electron density of the molecule (Å^2); The coefficients α_2, β_2, and γ_2 at the B3PW91/6-31G(d,p) level are 4.43×10^{-4}, 2.0599, and -2.4825, respectively.[3]



(4)

Thermal stability was examined by calculating the bond dissociation energy (ΔE_{BD}) and the decomposition activation energy barrier ($\Delta E^{\neq}$) of all possible pyrolysis processes. The sensitivity was evaluated by predict the free space in the lattice (ΔV) [4, 5] and the maximum heat of detonation per unit volume (ρQ_{max})[4-6]. The formulas are as follows:

$$\Delta E_{BD}(A–B) = E_{A·} + E_{B·} - E_{A–B} \quad (5)$$

$$\Delta E^{\neq} = E_{TS} - E_{A–B} \quad (6)$$

$$\Delta V = V_{eff} - V_{int} \quad (7)$$

where A–B is the neutral reactant; A· and B· are the corresponding radical products after the dissociation of A–B bond; TS is the transition state in the pyrolysis process; $E_{A·}$, $E_{B·}$, $E_{A–B}$, and E_{TS} are their corresponding total energies

after the correction of the zero-point energy; V_{eff} is the effective volume of the molecule that would corresponding to 100% packing of the unit cell, which is usually quite similar to the 0.001 au contour of the molecule's electronic density; V_{int} is the space encompassed by the 0.003 au contour of the molecule's electronic density.

The polymorph of **EC-1** was predicted by searching the molecular packings among seven most possible space groups (*C*2/*c*, $P2_1$, $P2_1/c$, *P*1, $P2_12_12_1$, *Pbca*, and $Pna2_1$) by using Dreiding force field[7] and Polymorph module of Materials Studio software[8]. The electrostatic and van der Waals interactions are selected to Ewald and Atom based, respectively.

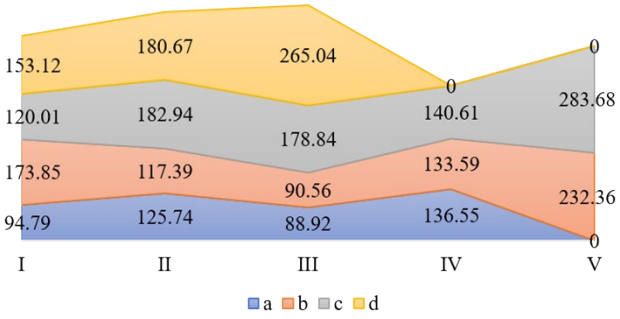


Figure S1. Reaction activation Gibbs free energy ($\Delta G^{\neq}$, in kJ.mol^{-1}) of each D–A reaction (**Series a-d**).

Table S1. $\Delta G^{\neq}_{\text{dist-diene}}$, $\Delta G^{\neq}_{\text{dist-dienophile}}$, $\Delta G^{\neq}_{\text{dist}}$, $\Delta G^{\neq}_{\text{int}}$, and $\Delta G^{\neq}$ (in kJ.mol^{-1}) of the D–A reactions between ethylene and 17 aromatic dienes, together with the NICS(0) and NICS (1) values (in ppm) of these dienes.

Dienes	$\Delta G^{\neq}_{\text{dist-diene}}$	$\Delta G^{\neq}_{\text{dist-dienophile}}$	$\Delta G^{\neq}_{\text{dist}}$	$\Delta G^{\neq}_{\text{int}}$	$\Delta G^{\neq}$	NICS(0)	NICS (1)
0N	63.74	25.80	89.54	5.25	94.79	-2.7260	-5.4644
1N-I	87.21	34.35	121.56	4.18	125.74	-2.7869	-6.7577
1N-II	63.32	22.39	85.71	3.20	88.92	-0.8175	-6.2295
1N-III	101.56	51.91	153.47	-16.92	136.55	-15.7534	-11.9220
2N-I	110.02	42.07	152.10	21.76	173.85	-3.1729	-7.9993
2N-II	88.21	30.02	118.23	-0.83	117.39	-1.3625	-7.4592
2N-III	70.93	22.47	93.40	-2.84	90.56	-0.0645	-7.1982
2N-IV	103.69	48.53	152.22	-18.63	133.59	-14.4206	-12.1437
2N-V	165.79	49.19	214.97	17.39	232.36	-15.3908	-13.0016
3N-I	92.51	25.73	118.24	1.76	120.01	-0.5641	-9.1562
3N-II	130.29	56.17	186.46	-3.52	182.94	-14.7492	-14.4732
3N-III	133.68	59.17	192.84	-14.00	178.84	-13.8860	-12.9131
3N-IV	116.96	47.20	164.16	-23.55	140.61	-13.0269	-12.5978
3N-V	210.95	47.84	258.79	24.89	283.68	-15.1184	-14.4956
4N-I	122.25	27.99	150.24	2.88	153.12	-5.0621	-10.5709
4N-II	142.69	54.20	196.89	-16.22	180.67	-14.1547	-14.8677

4N-III	198.73	46.12	244.84	20.20	265.04	-14.5034	-15.2727

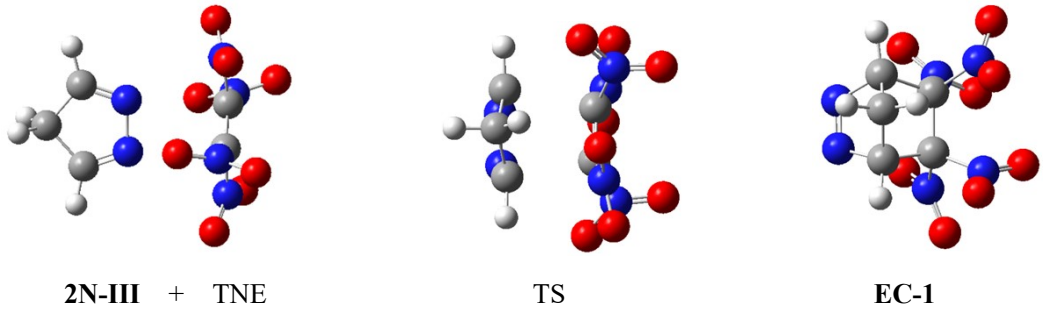


Figure S2. Optimized geometries of involving compounds in Reaction process of **EC-1**

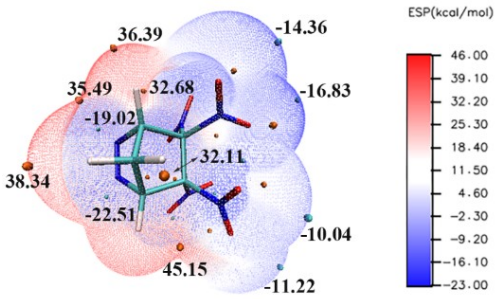


Figure S3. Electrostatic potential (ESP) on the 0.001 au molecular surface of **EC-1** (blue and red points denote the surface local minima and maxima, respectively).

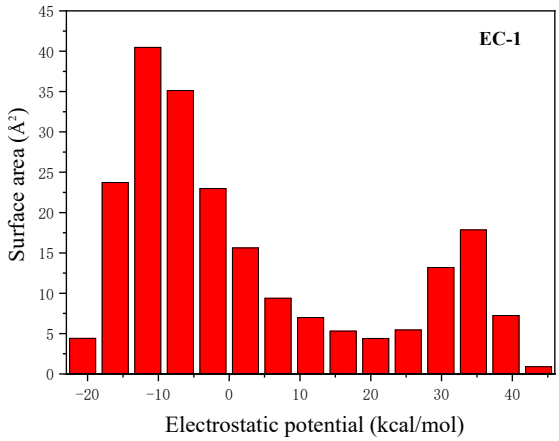


Figure S4. The area percent in electrostatic potential range of **EC-1**

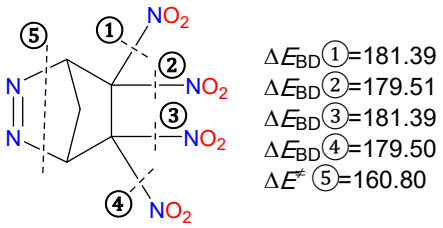


Figure S5. Possible pyrolysis processes for **EC-1**, together with the ΔE_{BD} and $\Delta E^{\neq}$, in kJ.mol^{-1}.

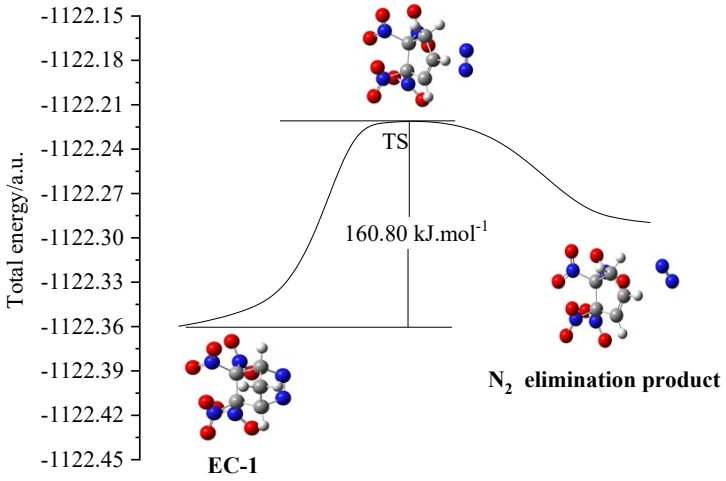


Figure S6. Energy profile and the optimized geometries of involving compounds during the most possible pyrolysis process (N_2 elimination process) of **EC-1**

Table S2. *OB* (%), ρ (g.cm^{-3}), $\Delta H_f°$(s) (kcal.mol^{-1}), *D* (km.s^{-1}), *P* (GPa), ΔV (Å^3), and ρQ_{max} (kcal.cm^{-3}) of **EC-1**, *trans*-**BIT,** and RDX.

	OB	ρ	$\Delta H_f°$(s)	*D*	*P*	ΔV	ρQ_{max}
EC-1	-23.18	1.89	36.99	8.851	35.8	47	2.70
Trans-**BIT**[9]	0	2.06	-95.28	9.473	42.2	72	3.08
RDX[10]	-21.61	1.82	18.9±1.2	8.754	34.7	46	2.71

Table S3. Cell parameters predicted with Dreiding force field for **EC-1**

parameters	*C*2/*c*	*P*1	$P2_1$	$P2_1/c$	$P2_12_12_1$	*Pbca*	$Pna2_1$
Z	8	2	2	4	4	8	4
ρ(g.cm^{-3})	1.85	1.87	1.86	1.86	1.90	1.87	1.84
E(kcal.mol^{-1}.cell^{-1})	43.32	42.69	42.88	42.76	42.16	43.08	43.18
a(Å)	16.72	12.66	6.55	7.90	11.44	7.87	13.41
b(Å)	14.10	7.14	11.01	22.55	6.82	11.02	6.55
c(Å)	12.09	6.46	6.85	7.10	12.40	22.68	11.33
α (°)	90	108.11	90	90	90	90	90
β (°)	44.11	117.88	90.83	51.03	90	90	90
γ (°)	90	78.71	90	90	90	90	90

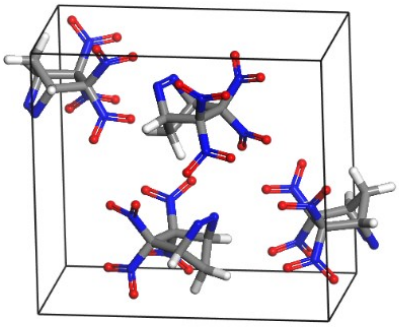


Figure S7. The most possible crystal packing of **EC-1** predicted by using Dreiding force field.

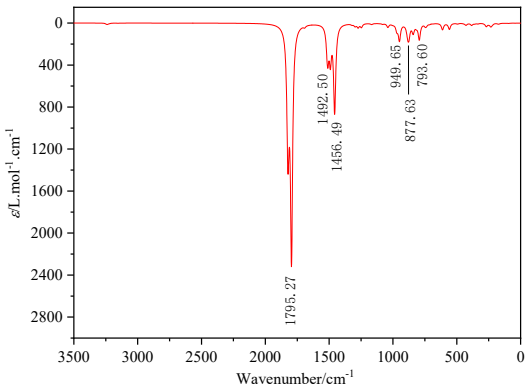


Figure S8. The predicted IR spectrum of **EC-1** at the M06-2X/6-31G(d) level.

The IR spectrum was predicted at the M06-2X/6-31G(d) level, with a scale factor of 0.947. For the complexity of vibration modes, only some characteristic vibration modes are assigned here. In **EC-1**, 1795.27 cm^{-1} belongs to NO_2 antisymmetric stretching vibration, 1492.50 cm^{-1} to CH_2 shear vibration, 1456.49 cm^{-1} to NO_2 symmetric stretching vibration, 793.60-949.65 cm^{-1} to deformation vibration of the molecular skeleton.

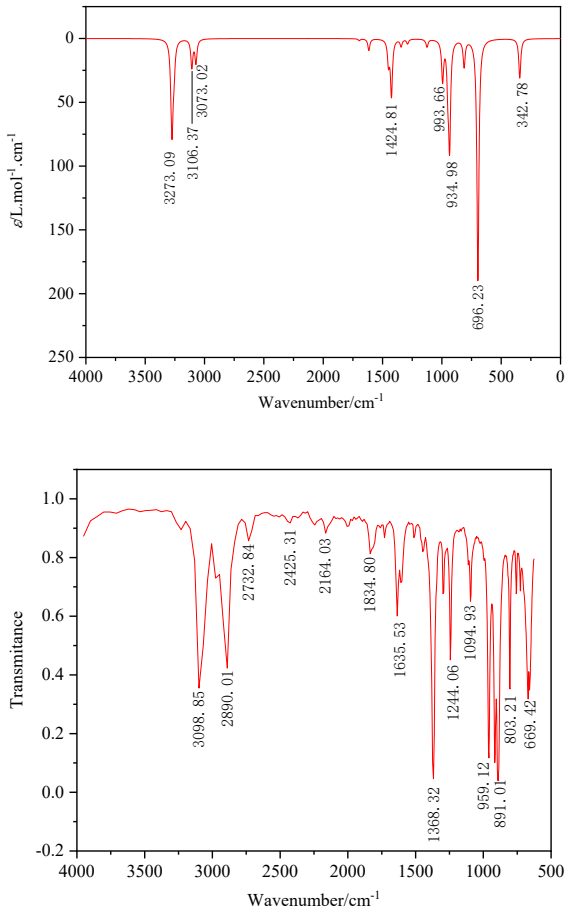


Figure S9. The predicted IR spectrum of cyclopentadiene (**0N**) at the M06-2X/6-31G(d) level (up) and its experimental IR spectrum (bottom)

In comparison with the predicted and experimental IR spectra of cyclopentadiene (**0N**), we can see that the IR spectrum of **0N** predicted at the M06-2X/6-31G(d) level was a little bit blue shifted. It suggests that the IR spectrum of **EC-1** predicted at the M06-2X/6-31G(d) level (**Figure S8**) may also a little bit blue shifted.

The Cartesian coordinates of all involved compounds in the reaction process of EC-1 optimized at the M06-2X/6-31G(d) level

Frequency calculations ensure that reactants and products do not have any imaginary frequency and transition states (TSs) have only one imaginary frequency.

Reactant, i.e., 2N-III + TNE

C	-0.96704300	-0.65953700	0.01561300
C	-0.96728400	0.65928900	-0.01563000
N	1.73479500	0.55303900	-0.45386900
N	1.73497300	-0.55246500	0.45390000
N	-0.93296600	-1.43416100	1.26346900
O	-1.19895900	-0.83002300	2.27779100
O	-0.64479900	-2.60141000	1.14722900
N	-0.96194000	1.53311200	1.17596700
O	0.08626100	1.67070800	1.75170700
O	-2.02877500	2.04972400	1.41166500
N	-0.93357600	1.43392200	-1.26348500
O	-1.19893300	0.82953900	-2.27783700
O	-0.64631400	2.60138800	-1.14725700
N	-0.96141900	-1.53342500	-1.17594700
O	0.08682400	-1.67084200	-1.75162200
O	-2.02813100	-2.05031200	-1.41161200
C	3.92818200	0.00059500	-0.00002400
H	4.57714100	-0.56133800	-0.68271600
H	4.57637000	0.56305800	0.68300300
C	2.94608000	-0.87015000	0.71432400
H	3.17805900	-1.69070200	1.38400900
C	2.94581000	0.87097400	-0.71443400
H	3.17749000	1.69160600	-1.38412800

TS

C	0.67242500	0.14869700	0.29718000
C	-0.67605900	0.30376900	0.08288200
N	-0.72903700	-2.22570700	-0.84079700
N	0.60281800	-2.34425800	-0.73950600
N	1.66597900	1.23715800	0.01527700
O	1.65544000	2.11198300	0.84597500
O	2.38403100	1.14029900	-0.95009000
N	-1.17472300	1.49768100	-0.64139900
O	-0.36298400	2.13088000	-1.28746900
O	-2.35876500	1.71957200	-0.55036000
N	-1.72085600	-0.08167700	1.10779600
O	-1.63325700	0.57318500	2.12040100
O	-2.55484100	-0.89244000	0.81106800
N	1.15508100	-0.70341700	1.40027500

O	0.33533100	-1.42789800	1.91553700
O	2.33733800	-0.62249600	1.64826000
C	0.20332300	-0.68252000	-2.29909800
H	0.23114100	-1.19786600	-3.27380900
H	0.33858500	0.38364600	-2.47389400
C	1.18801800	-1.35903800	-1.41252800
H	2.26844000	-1.30065500	-1.46999500
C	-1.02017100	-1.15468300	-1.58362100
H	-2.05657700	-0.94561800	-1.82927300

Product, i.e., EC-1

C	-0.78055100	-0.06189500	0.04756600
C	0.76538000	0.08829500	0.13088700
N	0.70288400	-1.99348900	1.38852200
N	-0.52999900	-2.08132300	1.33622900
N	-1.50096500	1.25533500	-0.20196100
O	-1.21699600	1.79378100	-1.24313600
O	-2.28378500	1.61752300	0.64186900
N	1.28525600	1.53904100	0.17338300
O	0.60366600	2.35545300	0.75260900
O	2.38788800	1.70497800	-0.28105500
N	1.53035800	-0.51413100	-1.03417400
O	1.23050000	-0.06946400	-2.11565800
O	2.38107300	-1.32145200	-0.75766700
N	-1.31731200	-0.98619100	-1.05289200
O	-0.61291100	-1.90111400	-1.39923900
O	-2.45802200	-0.76298100	-1.38101000
C	-0.11010700	-0.02157200	2.34710700
H	-0.12321600	-0.46318200	3.34530800
H	-0.20992600	1.06087300	2.40306900
C	-1.11847800	-0.69541400	1.41943200
H	-2.18099100	-0.70125100	1.64645200
C	1.07197600	-0.53673700	1.51647800
H	2.10196000	-0.40098300	1.83889500

The Cartesian coordinates of all involved compounds in the N_2 elimination process of EC-1 optimized at the M06-2X/6-31G(d) level

Frequency calculations ensure that reactants and products do not have any imaginary frequency and transition states (TSs) have only one imaginary frequency.

EC-1

C	-0.78055100	-0.06189500	0.04756600
C	0.76538000	0.08829500	0.13088700
N	0.70288400	-1.99348900	1.38852200
N	-0.52999900	-2.08132300	1.33622900
N	-1.50096500	1.25533500	-0.20196100
O	-1.21699600	1.79378100	-1.24313600
O	-2.28378500	1.61752300	0.64186900
N	1.28525600	1.53904100	0.17338300
O	0.60366600	2.35545300	0.75260900
O	2.38788800	1.70497800	-0.28105500
N	1.53035800	-0.51413100	-1.03417400
O	1.23050000	-0.06946400	-2.11565800
O	2.38107300	-1.32145200	-0.75766700
N	-1.31731200	-0.98619100	-1.05289200
O	-0.61291100	-1.90111400	-1.39923900
O	-2.45802200	-0.76298100	-1.38101000
C	-0.11010700	-0.02157200	2.34710700
H	-0.12321600	-0.46318200	3.34530800
H	-0.20992600	1.06087300	2.40306900
C	-1.11847800	-0.69541400	1.41943200
H	-2.18099100	-0.70125100	1.64645200
C	1.07197600	-0.53673700	1.51647800
H	2.10196000	-0.40098300	1.83889500

TS

C	-0.05138100	-0.78583400	0.20304700
C	-0.04364900	0.78521700	0.15059200
N	2.80555000	0.58327000	0.74124100
N	2.80707400	-0.53422200	0.75954100
N	-1.51385700	-1.31886400	0.42002000
O	-2.15529900	-0.72718100	1.26678300
O	-1.82311800	-2.32251400	-0.15935800
N	-1.48346900	1.35472900	-0.07777000
O	-1.86252200	2.19397900	0.69409200
O	-2.05447700	0.90218000	-1.03986500
N	0.71002600	1.43511100	-1.03506400
O	1.53924900	0.78140800	-1.61417200
O	0.43993300	2.60131400	-1.20146500
N	0.38719000	-1.50870400	-1.07042000

O	1.23025700	-2.36041000	-0.93141600
O	-0.19840100	-1.18960300	-2.07310700
C	0.65743000	0.04870000	2.27872200
H	1.21929800	0.08503600	3.20974100
H	-0.45103000	0.01088400	2.52789400
C	0.68425800	-1.14326800	1.45390900
H	0.70312100	-2.16478700	1.80961500
C	0.58734900	1.21274400	1.42046300
H	0.61199000	2.25087700	1.71759200

N_2 elimination product

C	0.53407800	-0.74511500	-0.22465400
C	0.00304000	0.70508800	-0.15773100
N	-4.04856900	0.04824200	-0.50015800
N	-4.33250100	-0.97725200	-0.22624500
N	1.93881900	-0.75095100	-0.86287700
O	2.02014600	-0.07098800	-1.86376400
O	2.78405200	-1.44330900	-0.36404000
N	1.07576800	1.77124400	-0.06360900
O	0.80984300	2.82835000	-0.58462900
O	2.07182400	1.48224700	0.55742200
N	-0.85636000	0.88920700	1.09504800
O	-1.66520900	0.00624600	1.28344200
O	-0.70752800	1.90171500	1.72662400
N	0.70282700	-1.43388900	1.11757500
O	0.56240400	-2.63358200	1.10552900
O	0.99392700	-0.73097500	2.05681400
C	-1.18450200	-0.55927200	-1.77849200
H	-1.92616200	-0.81179900	-2.52811800
H	-0.36292000	1.40234600	-2.16290900
C	-0.41453700	-1.44168600	-1.14855400
H	-0.38345700	-2.51664600	-1.26545000
C	-0.91029400	0.86496800	-1.38342200
H	-1.80973600	1.43837400	-1.14372500

References

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